



AN ASSESSMENT OF ATMOSPHERIC PCB LEVELS IN MISSISSAUGA

prepared by

ONTARIO **RESEARCH**
FOUNDATION

for



Ministry
of the
Environment

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An Assessment of Atmospheric PCB Levels
in Mississauga
[Report No. P-2818/G (Revised) -01]
for
Ministry of the Environment
Province of Ontario

S.C. Barton
G.H.S. Thomas
N.D. Johnson

November 15, 1978

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An Assessment of Atmospheric PCB Levels
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SUMMARY

A comprehensive ambient air survey of polychlorinated biphenyls (PCBs) in the area surrounding St. Lawrence Cement Company Limited and Tricil Limited in Mississauga, Ontario, was conducted during the months of June and July, 1978. Monitoring sites were located immediately adjacent to these industrial operations and in the residential areas northwest to northeast of the plant. Average concentrations at the plant property monitoring sites ranged from 9 to 36 ng.m^{-3} with the highest levels occurring to the northeast of the Tricil plant. Contaminated storage and handling areas were identified as probable sources of the ambient PCB levels measured at these sites.

Average concentrations at the residential sites ranged from 6 - 12 ng.m^{-3} . Although no air quality criteria have yet been established for PCBs, it was considered useful to compare individual values with levels of 10 to 20 ng.m^{-3} to determine the distribution of values observed. While approximately 31% of the samples exceeded 10 ng.m^{-3} , only 10% were in excess of 20 ng.m^{-3} . Several features of the data suggest that the high levels measured on occasion at certain sites probably were due to positive interferences by non-PCB materials.

There was no tendency for high levels to occur concurrently at a number of stations, nor at any particular time during the study. Comparison of PCB concentrations at upwind and downwind sites, and correlations of PCB concentrations with wind direction, showed that neither St. Lawrence Cement nor Tricil emissions made a measurable contribution to ambient PCB levels in the residential areas surrounding the plants under the operating and atmospheric conditions prevailing during the course of

this study. However, low level fugitive emissions of chlorinated material were apparent at the plant property sites and indicated that losses from storage and handling areas is the most likely source of PCBs at the plant properties.

1. INTRODUCTION

Commercial polychlorinated biphenyls (PCBs) are prepared by direct chlorination of biphenyl. This procedure results in complex mixtures containing numerous isomers of chlorobiphenyls with different chlorine contents. Desirable properties such as thermal stability, non-flammability and excellent electrical insulating ability has resulted in a wide variety of applications and, consequently, numerous pathways whereby PCBs can be introduced into the environment have been established. Loss of PCBs to the environment may occur during their production, transport, storage, incorporation into products, use and disposal. Incineration is considered to be one of the more attractive disposal methods, provided that temperatures in excess of approximately 1200°C for a 2-second dwell time are maintained (1). Not only does this technique permit the heat value of the compounds to be utilized, but it also minimizes the need to use less desirable non-destructive disposal techniques such as dumping at sanitary landfill sites and at sea.

Atmospheric PCBs may be found in the vapour phase, in the form of an aerosol, or adsorbed onto particulate matter. Highest levels are observed in urbanized and industrialized areas and atmospheric transport in these various forms is the major pathway by which PCBs are carried to locations distant from their source. Only limited data are available on atmospheric levels in industrialized inland areas. Preliminary results obtained in recent Canadian (2) and U.S. (3) studies suggest that PCB levels can be as high as $30\text{--}50\text{ ng.m}^{-3}$ and may typically be several ng.m^{-3} . Berg et al (2) also concluded that the majority of PCBs occur as vapours in the atmosphere.

In a more recent U.S. study (4) to develop new sampling and analytical methods, airborne PCB concentrations were measured over the range of 4 ng.m^{-3} to 1400 ng.m^{-3} . Samples were collected near an electric power substation and transformer storage facility, and at a landfill site which had been formerly used as a disposal site for rejected capacitors and other PCB-containing wastes. Levels at the substation ranged from $11\text{--}44\text{ ng.m}^{-3}$. Much higher levels (up to 1400 ng.m^{-3}) were detected at the landfill site.

A concern recently has developed regarding atmospheric levels of PCBs in the Mississauga area. Some of the waste solvents burned by the St. Lawrence Cement Company as supplemental fuel have been found to contain trace amounts of PCBs, and wastes incinerated by Tricil Limited have been found to contain lesser amounts of PCBs. Release of PCBs could occur from incomplete combustion, during material handling, or as a result of process upset and spillage. In order to establish prevailing PCB concentrations in the immediate vicinity of the plants, and in the residential areas in which plant emissions might contribute to ambient levels, an ambient air survey was conducted during June and July, 1978. The specific objectives of the work undertaken were:

- to monitor ambient levels of PCBs in the immediate vicinity of the plants in order to identify any fugitive emissions which might occur during the handling of materials contaminated with PCBs
- to monitor ambient levels of PCBs at representative sites in the residential areas surrounding the plants
- to correlate ambient PCB levels with meteorological data and plant operating conditions in order to define the extent to which these industrial operations may contribute to ambient concentrations of PCBs.

2. SAMPLING AND ANALYTICAL METHODOLOGY

2.1 Locations

Eleven monitoring sites were selected at which to collect 24-hour average air samples. Two distinct sets of stations were established:

- 4 "fence line" sites on the property of the plants (including one adjacent to the plants),
- 7 sites distributed throughout the residential areas north of the plants.

Site locations are shown in Figure 2.1 and brief descriptions are given in Table 2.1. The southwesterly winds which prevail during the summer months were taken into account in selecting the sites. Four stations were located adjacent to or within the industrial properties as follows:

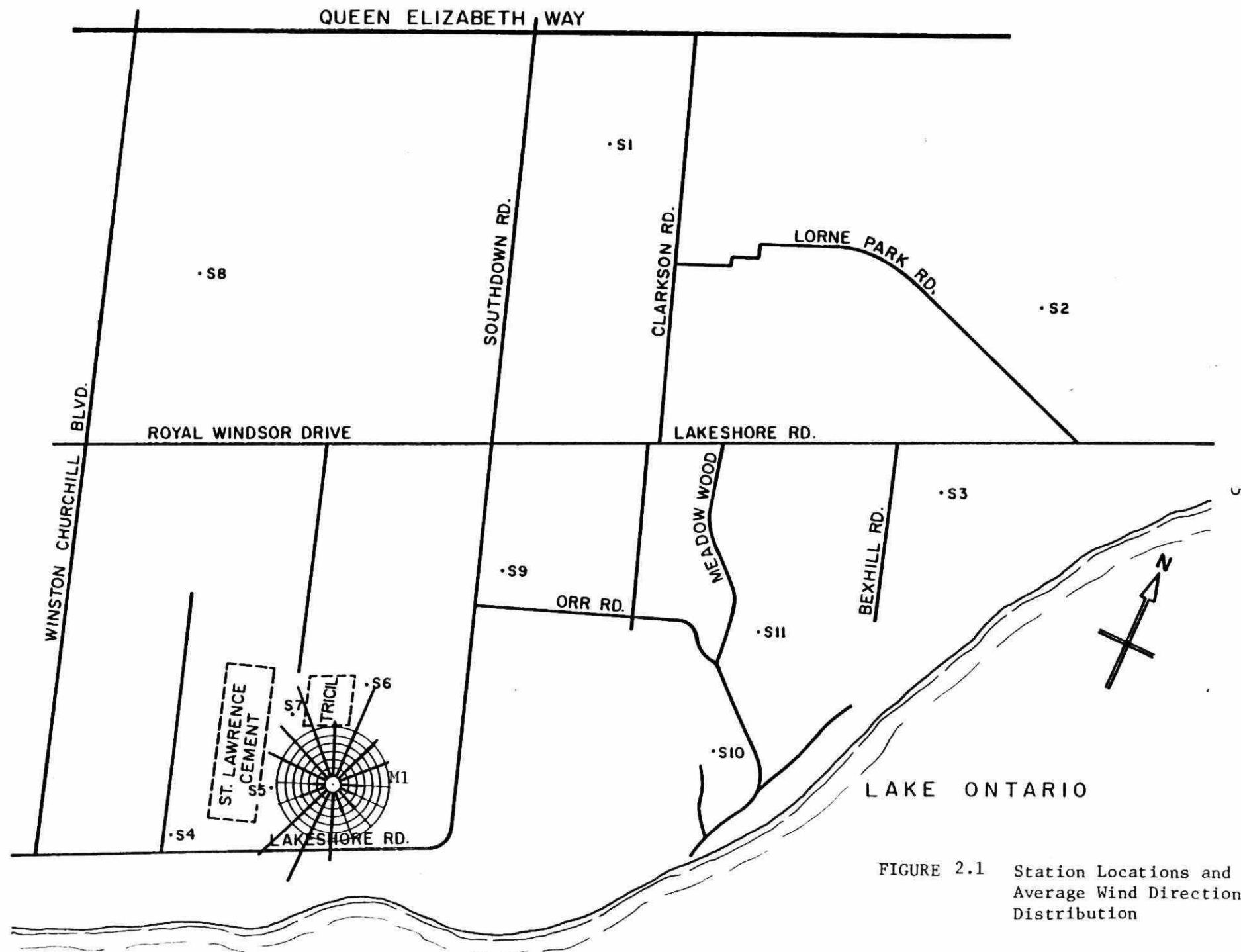


FIGURE 2.1 Station Locations and Average Wind Direction Distribution

TABLE 2.1

LOCATIONS OF SAMPLE STATIONS IN MISSISSAUGA AREA

Station Number	Location (Address)	Position	Approx. Height Above Ground (m)
	<i>Mr. Ted Walter / 822-1383</i>		
1	Private Residence 1538 Springwell	Rooftop	3
2	Private Residence <i>Mr. Tapley</i> 1159 Wildfield Cres.	<i>274-4694</i> Ground level, back of house	1-1/2
3	Private Residence <i>Mrs. Darling</i> 866 Parkland	Ground level, side of house <i>822-0798</i>	1
4 *	Motel 2477 Lakeshore Rd.	Rooftop	3-1/2
5 **	St. Lawrence Cement Co. Lakeshore Rd.	Rooftop, east side of office building (previous guardhouse)	3
6 **	Tricil 551 Avonhead Rd.	Ground level, east fence, behind plant, near north corner	1-1/2
7 **	Tricil 551 Avonhead Rd.	Ground level, west fence, in front of plant, near north corner	1-1/2
8	St. Helens Public School Bodley St.	Rooftop	6
9	Private Residence <i>Mr. C. Durkhan</i> 2012 Carrera	Ground level, back of house	1-1/2
10	Private Residence <i>Mr. H. B. B. B.</i> 473 Apple Lane <i>822-9747</i>	Ground level, back of house	1
11	Green Glade Public School 1550 Green Glade Ave.	Rooftop	7

* Located adjacent to St. Lawrence Cement Co. property

** Located on industrial properties

upwind of both St. Lawrence Cement and Tricil, on St. Lawrence Cement property, between St. Lawrence Cement and Tricil (Tricil SW fence-line) and downwind of both St. Lawrence Cement and Tricil (northeast Tricil fence-line). The remainder of the stations were located in the residential districts at various distances from about 1.3 to 4.5 km from the industries. The sampler inlet was positioned at a height of about 1m (tables at ground level) to about 6m (rooftops).

The meteorological station was located on the roof of the blower building at the MOE Clarkson Wastewater Treatment Plant (see Figure 2.1) at an elevation of about 12m. Wind direction and speed were recorded continuously using a portable MRI anemometer and decoded as hourly averages. Tabulated hourly average wind direction and speed at 43m elevation were also obtained from Ontario Hydro (at the nearby Lakeview Station) for comparative purposes throughout the survey.

2.2 Sampling Equipment and Procedures

The sampling equipment used at each site included a Nutech gas train (Model 221-1A14 A4DC) consisting of a 12V AC/DC gas pump, dry gas meter, flowmeter and timer mounted in a weatherproof enclosure (see Figure 2.2). The dry gas meters were previously calibrated at the MOE laboratory using a wet test meter and found to have a flowrate precision within $\pm 2\%$. The adsorbent collector tube contained a quantity of Florisil (~ 2.5 to 3.0 g) held in a glass tube, as described in Section 2.3.2 giving an adsorbent bed size of about 1.3 cm diameter and 4 cm height. The ends of the tube were sealed during transit using a teflon-lined screw cap at one end and a brass and teflon Swagelok fitting at the other end. All components of the collector tubes were prewashed with hexane to avoid contamination.

Battery power was required for the Nutech units at the two Tricil locations and was supplied at each site using two 12 volt batteries (charged daily) connected in parallel.

Twenty-four hour integrated ambient air samples were collected daily for nearly two months, with samples being changed at mid-day, the exact time depending on the station visit schedule. About 10 to 15 m^3 of air was passed through the collector tubes at the maximum flowrate (about 7 to 11 lpm). The collector tube joint and sampling trains were leak-checked

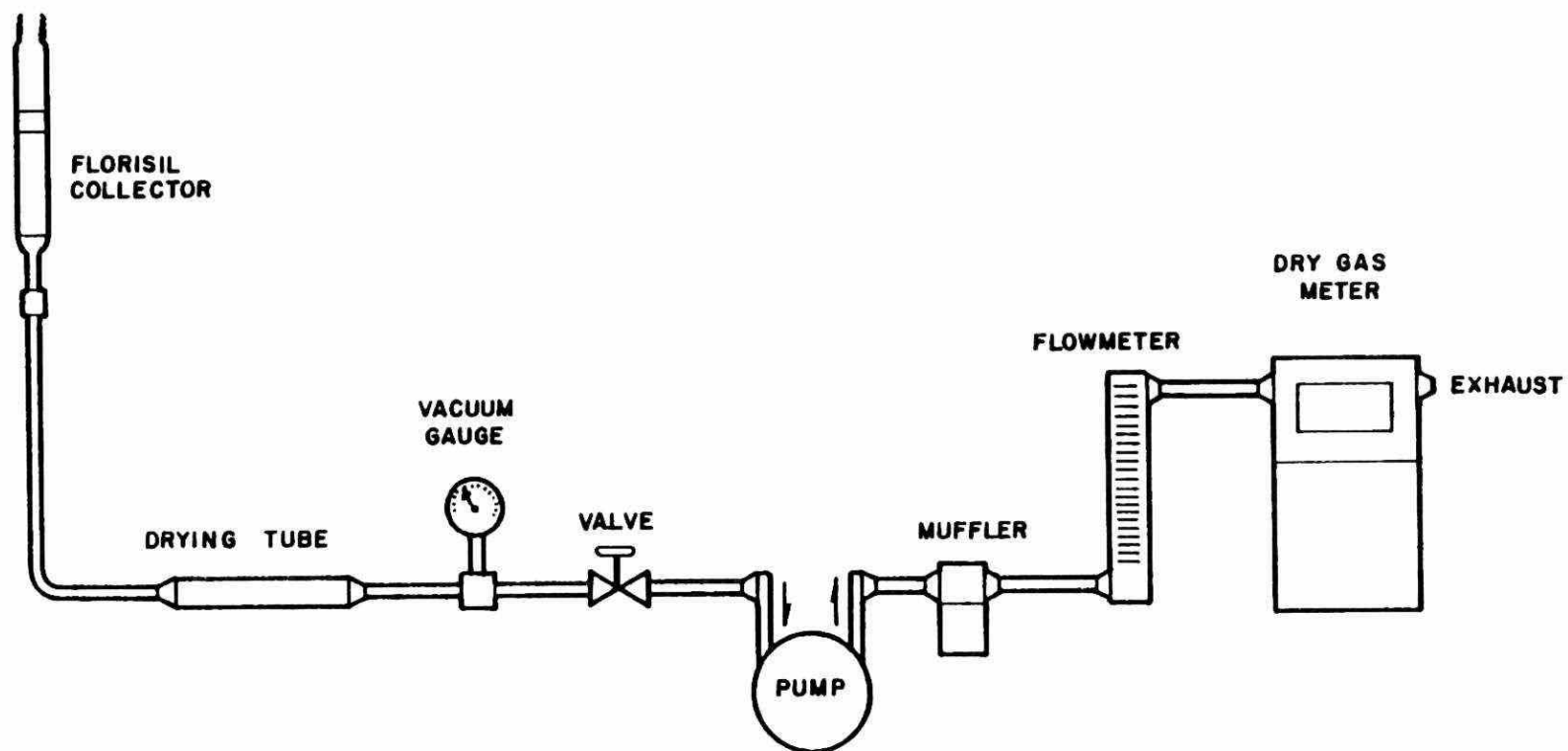


FIGURE 2.2 Ambient Air Nutech Sampling Train

prior to sampling by sealing the inlet with the teflon-lined cap and detecting a flowrate under a vacuum of about 18" mercury. During transit the capped tubes and blanks were stored in sealed glass jars. Sampling flowrates and meteorological condition records were maintained by field staff.

2.3 Analytical Procedures

2.3.1 Reagents

- (a) Sodium sulphate, anhydrous granular, analytical grade.
- (b) Sodium carbonate, anhydrous granular, analytical grade.

Both above solids soaked twice for 1 hour with acetone/benzene (9:1), drained and dried by suction, then oven dried for twenty-four hours and washed with hexane. This material was used providing that a GC-EC profile of the hexane extract was free of interferences.

- (c) Hexane (glass distilled - Caledon) used directly.
- (d) Methylene chloride (glass distilled - BDH) used directly.
- (e) Florisil, pesticide grade, 60/100 mesh (Floridin Co.), heated to 300°C and then deactivated with 2% H₂O in hexane.
- (f) Florisil, 30/60 mesh (Floridin Comp.), treated as outlined in text prior to use.

2.3.2 Pre-and Post Treatment Sampling Tubes

Florisil (30/60 mesh), a product of Floridin Company, was used as a collecting adsorbent and was pretreated in the following manner. Florisil (30g) was placed in an extraction thimble (9cm x 3cm I.D.) and held in place with a glass wool plug. The thimble was placed in a soxhlet apparatus which was extracted as follows:

1. 48 hours with methylene chloride.
2. 24 hours with hexane.

The Florisil was removed from the thimble and air dried. The dried Florisil was poured into a glass tube (14 cm x 1.3 I.D.) sitting on a glass wool plug to a depth of 4cm and held in place with a glass wool plug on top.

The following protocol with respect to solvent elution and activation was performed with all Florisil filled tubes:

1. Methylene chloride (200ml) - discard.
2. Hexane (300ml) - discard.
3. Hexane (100ml).
4. Florisil tube activated by heating overnight at 130°C in an oven.

The final hexane eluate (100ml) was concentrated to incipient dryness and any residue taken up in hexane (1ml).

An aliquot (5 µl) of the concentrate was chromatographed using electron capture detection under normal PCB operating conditions. From the GC-EC profile produced, a decision was made regarding the acceptability of the tube for use in ambient sampling. The decision was made by "eyeballing" the GC profile and comparing it initially with a profile obtained with a standard Aroclor mixture (1248; 10 ng/ml) and subsequently with the use of pure isomers.

In order to fulfill the ambient tube preparation requirements (12 per day plus 36 for weekend use) within the time constraints of the programme, complete removal of PCB from the Florisil tubes could not be accomplished. The tubes were therefore assessed on the basis of an acceptable blank. Tubes that did not fulfill this requirement were eluted with additional solvent and if still judged unacceptable they were discarded.

Upon return to the laboratory, the tubes were eluted with hexane (100ml), the extract concentrated to incipient dryness and any residue taken up in hexane (5ml). The solution was transferred to a vial (10ml capacity) which was sealed and placed in a freezer (4°C) to await analysis by gas chromatography.

2.3.3 Gas Chromatography

(a) The gas chromatograph was a Hewlett Packard 5700A fitted with an automatic sampler (7671A). Digital integration of the electrometer output was achieved with the use of a Spectra Physics SP4020 data interface connected to a Spectra Physics SP4000 Central Processor.

Column	Glass coil (2m x 6mm O.D.)
Packing	3% OV101/6% OV210 on Chromosorb W (HP)
Injector Temperature	250°C
Detector Temperature	350°C
Column Temperature	215°C
Detector	Ni ⁶³ linearized EC
Gas Flowrate	Argon/5% methane at 60ml/min

(b) The gas chromatograph used was a Varian Model 3700. Digital integration of the electrometer output was achieved with the use of a Spectra Physics SP4020 data interface and a SP4060 remote terminal connected to a Spectra Physics SP4000 Central Processor.

Column	Glass U (1m x 2mm I.D.)
Packing	5% OV101 on Chromosorb G (HP: 100/120 mesh)
Injector Temperature	250°C
Detector Temperature	300°C
Column Temperature	190°C
Detector	Ni ⁶³ linearized EC
Gas Flowrates	N ₂ ~ 30 ml/min.

2.3.4 Quantitation

For routine monitoring of environmental samples for PCBs, packed column gas chromatography using electron capture detection (ECD) is the method of choice. The ECD response is not directly proportional to the chlorine content of the chlorobiphenyl molecule. In general the ECD response increases strongly for compounds with one to three atoms of chlorine per molecule, whereas only a small increase is recorded for those with four or more chlorine atoms. This difference in response is

very apparent with the higher and lower Aroclor mixtures. Because of this, the choice of an Aroclor as a quantitation reference can significantly affect the analytical result. For this reason extreme care and good judgement are imperative when the ECD is used for quantitation of PCB residues. Thus quantitation of PCBs is a complex problem, because of the multicomponent nature of PCBs and the industrial use of different commercial mixtures complicate the analysis.

Most routine quantitative procedures for PCB analysis have been based on comparison with standard commercial PCB preparations and if the GC-EC chromatogram resembles a standard Aroclor mixture this approach presents no difficulty. However, such quantitation by direct comparison of an unknown ECD chromatogram can be difficult because individual peaks in environmental samples are sometimes obscured by other components (even after clean-up), are completely missing, or have considerably different relative intensities. When the PCB residue is altered in some fashion from the commercial PCB, or when the residue appears to be derived from more than one Aroclor, then the best means of quantitation becomes less certain.

The method of quantitation finally adopted for this project evolved during the progress of the programme. Initially, when viewing the sample chromatographic profiles it was apparent that comparison of them with known commercial Aroclor standards was not possible. While there were peaks (mainly in early portion of GC profile) with retention times similar to peaks present in the standard Aroclors, there was no pattern similarity between the samples and standards profiles. The adequacy of any comparison procedure for a multi-peak determination such as this depends on the similarity of the sample and standard chromatograms. Since ORF analysts were in the process of collecting a number of pure individual PCB isomers, the use of pure isomer retention time data together with exact weights of the isomers appeared to offer an attractive approach. It would enable a total amount of PCB to be calculated as the sum of all the individual isomer peaks.

It must be emphasized that this approach is still a comparison technique and is not an entirely reliable quantifying procedure.

It will give an upper limit PCB concentration which will be the actual value provided that all peaks measured are in fact PCB. Confirmation of identity of the peaks by other procedures is still required for positive identification. The occurrence of relatively large variations in the isomer amounts strongly suggests positive interferences by other organic materials having similar retention times.

As a first approach, 6 isomers (2 tri-, 2-tetra, a penta-, and a hexa-), which were well resolved chromatographically and also considered to be the major isomers present in Aroclor mixtures 1242/1254, were selected. However, after discussions with analytical chemists from the MOE Resources Road Laboratory, the number of isomers was expanded. Since the present survey was concerned with air samples and thus was likely to involve the more volatile isomers, it was agreed that the number of isomers used was to be expanded to include some lower chlorinated ones and fill in some of the gaps apparent in the GC-EC profile of the 6 isomer standard.

A total of 16 pure isomers, which when chromatographed gave 12 peaks were used. The peak numbers with corresponding isomer contents and weights are summarized below:

<u>Peak Number</u>	<u>Isomer(s)</u>	<u>Concentration (ng/ml)</u>
1	2,2' + 2,5	117.6
2	2,4 + 2,5,2'	51.9
3	2,5,3' + 2,4,5	47.5
4	2,4,2',5'	18.4
5	2,3,5,2'	16.7
6	2,5,3',4'	12.8
7	2,4,5,2',5	7.0
8	2,4,5,2',3' + 2,3,4,2',5'	15.0
9	3,4,3',4'	19.2
10	2,4,5,2',4',5'	19.0
11	2,3,4,2',4',5'	8.4
12	2,3,4,2',3',4'	10.2

GC-EC profiles for the 16 isomer calibration standard and selected Aroclor standards (1221, 1242, 1016, 1248 and 1254) which were produced on the Spectra Physics printer/plotter (SP 4050) are shown in Figures 2.3 - 2.8. Calculated values for the total PCB in the various Aroclor mixtures based on the 16 isomer calibration ranged from 85 - 100% theoretical for Aroclor 1242 through Aroclor 1254. The value for Aroclor 1221 was only 25% of the theoretical. However, the reported composition of Aroclor 1221 includes 51% mono-chlorobiphenyl and 11% biphenyl which must be added to the above figure since the calibration mixture does not contain biphenyl or mono-chlorobiphenyl.

In addition, aliquots from fourteen (14) selected samples were delivered to MOE for comparative checks between their method and ORF's for PCB quantification. Considering the media from which the sample was obtained (ambient air) and the low concentrations and type of compounds being measured, the agreement in most cases was well within the normal limits of such interlaboratory comparisons ($\pm 20\%$).

During the routine monitoring of samples the GC profiles were produced with strip chart recorders. Some representative GC profiles of blanks and sample chromatograms from all the sampling stations, plus one of the isomer calibration mixture are shown in Figures 2.9 - 2.22. Quantification was accomplished with a SP 4000 mini processor with all calculations being performed automatically, and the data produced on a SP 4050 printer to give the isomers found (retention time data) and their quantity. The individual contributions were then summed to give a total PCB in the sample.

A quality assurance programme involved the occasional treatment of the calibration isomer mixture as a normal sample. The isomer mixture (5ml) was diluted with hexane (95ml) and the solution evaporated to incipient dryness, taken up in hexane (5ml) and an aliquot (5 μ l) chromatographed as a sample. Recoveries were 95% or better, however, the major losses were attributable to isomer peak 1 (dichlorobiphenyl) and isomer peak 2 (di-+trichlorobiphenyl). The losses represented 25-30% for peak 1 and 15-20% for peak 2.

FIGURE 2.3 Chromatographic Profile of 16 Isomer Calibration Mixture

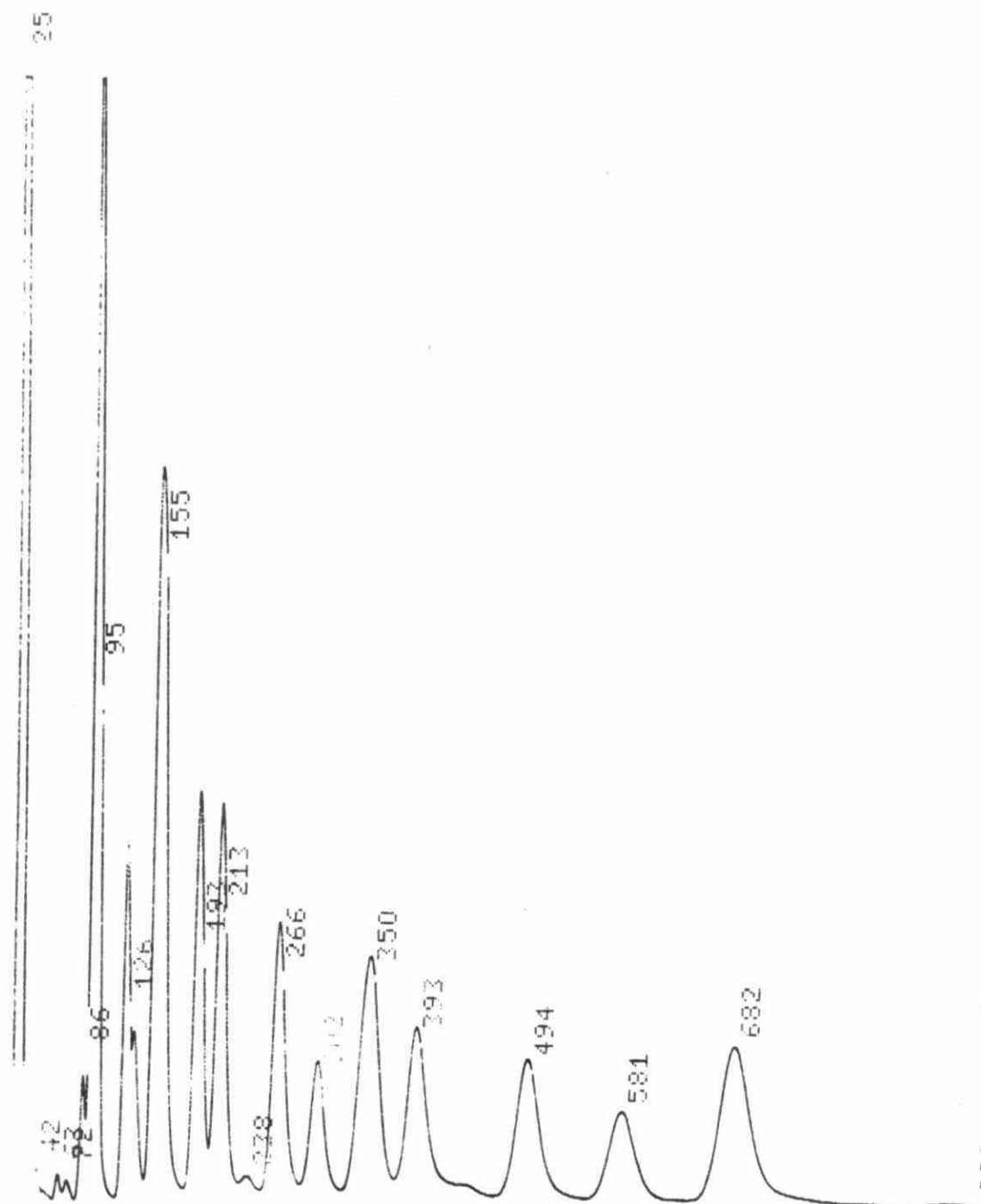


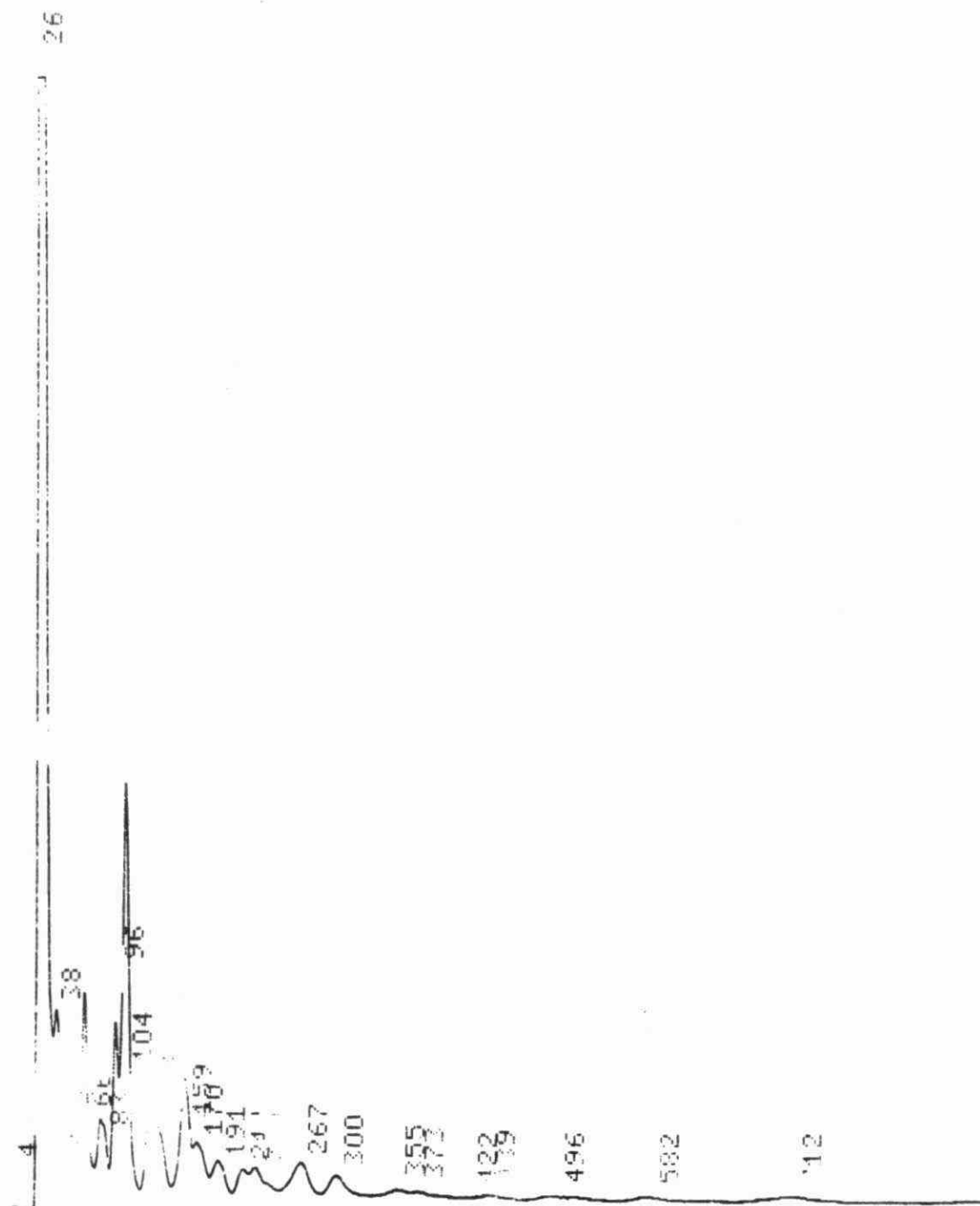
FIGURE 2.4 Chromatographic Profile of Standard Aroclor 1221 (0.2 μ g/ml)

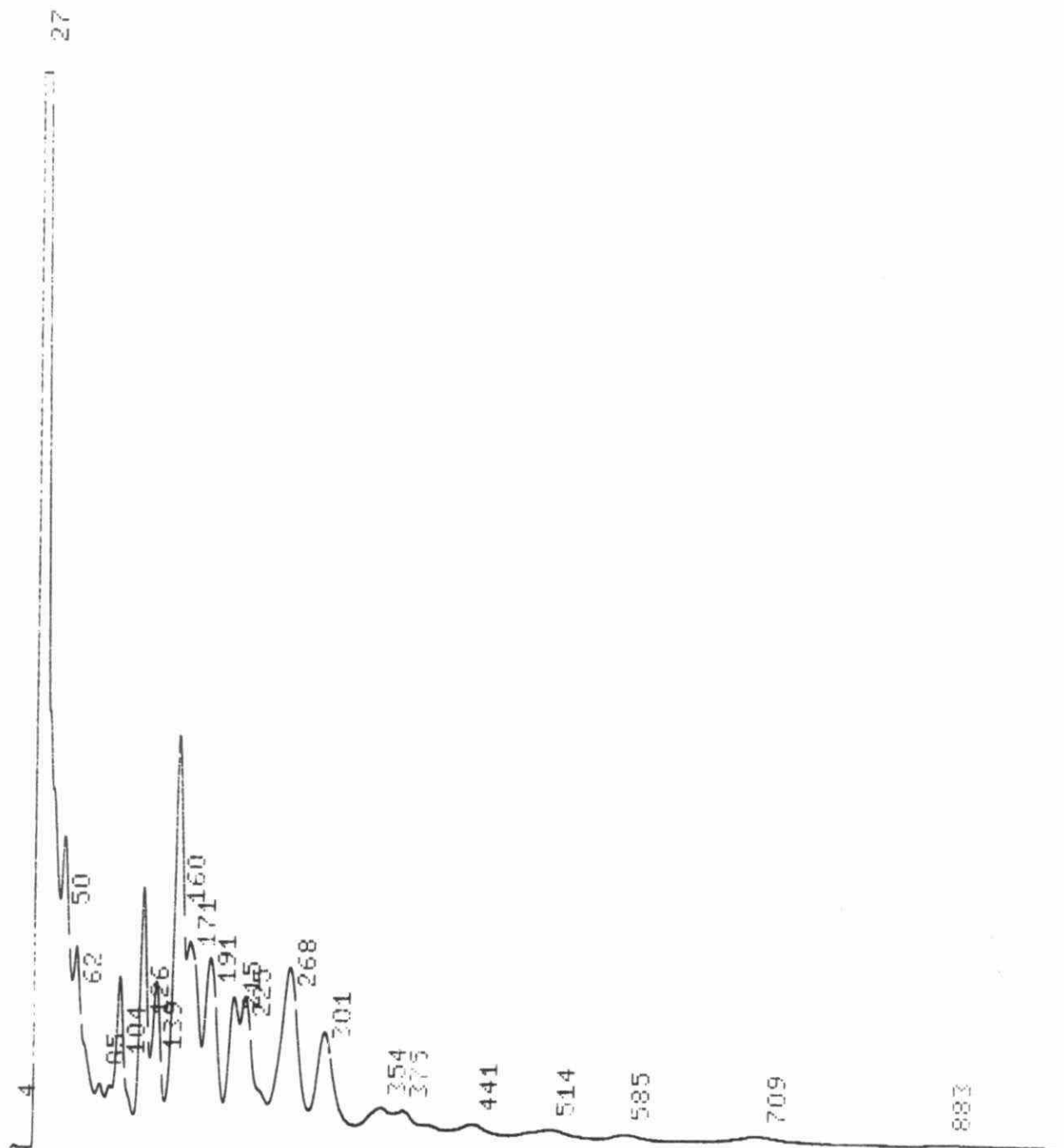
FIGURE 2.5 Chromatographic Profile of Standard Aroclor 1242 (0.1 μ g/ml)

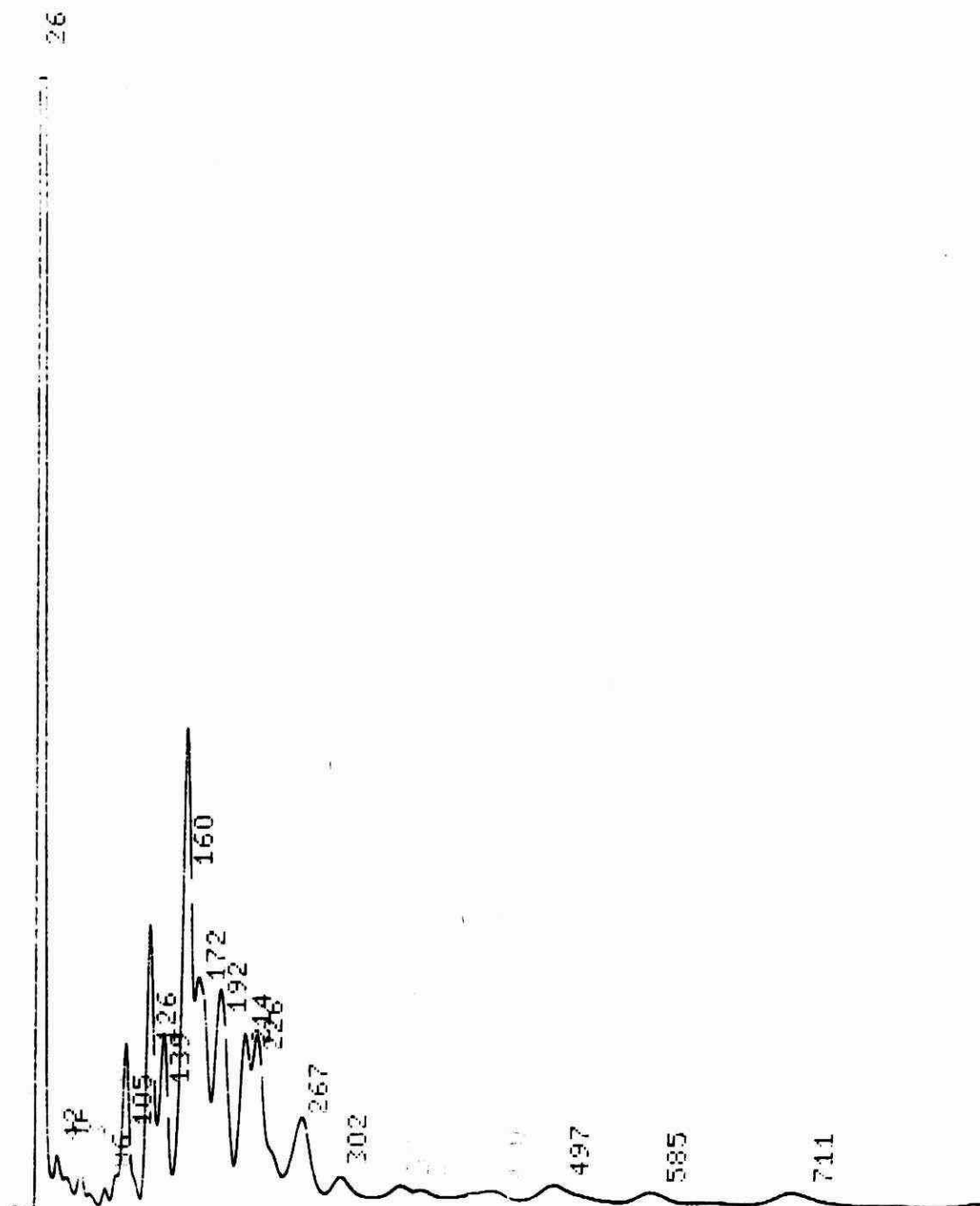
FIGURE 2.6 Chromatographic Profile of Standard Aroclor 1016 (0.1 μ g/ml)

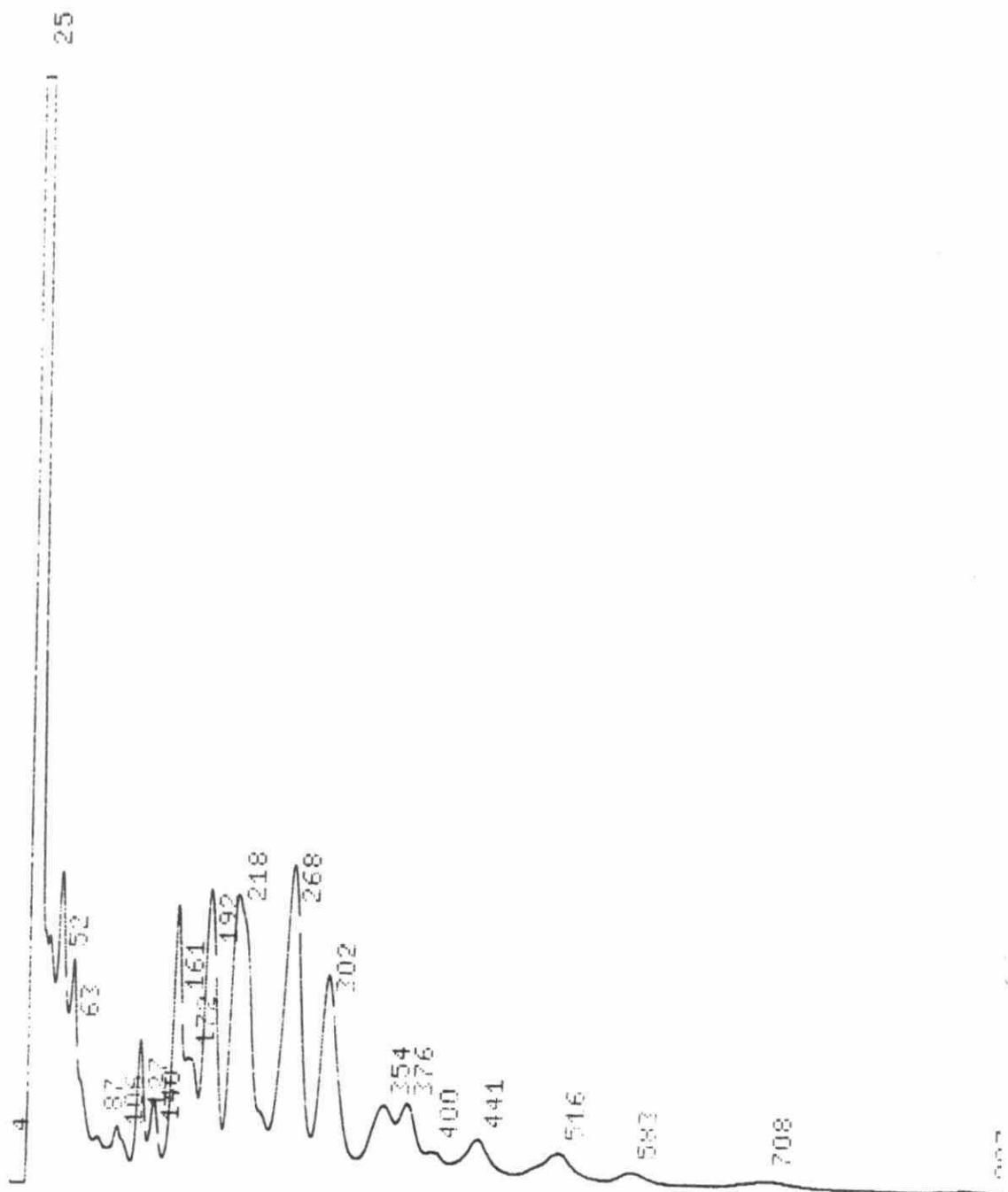
FIGURE 2.7 Chromatographic Profile of Standard Aroclor 1248 (0.1 μ g/ml)

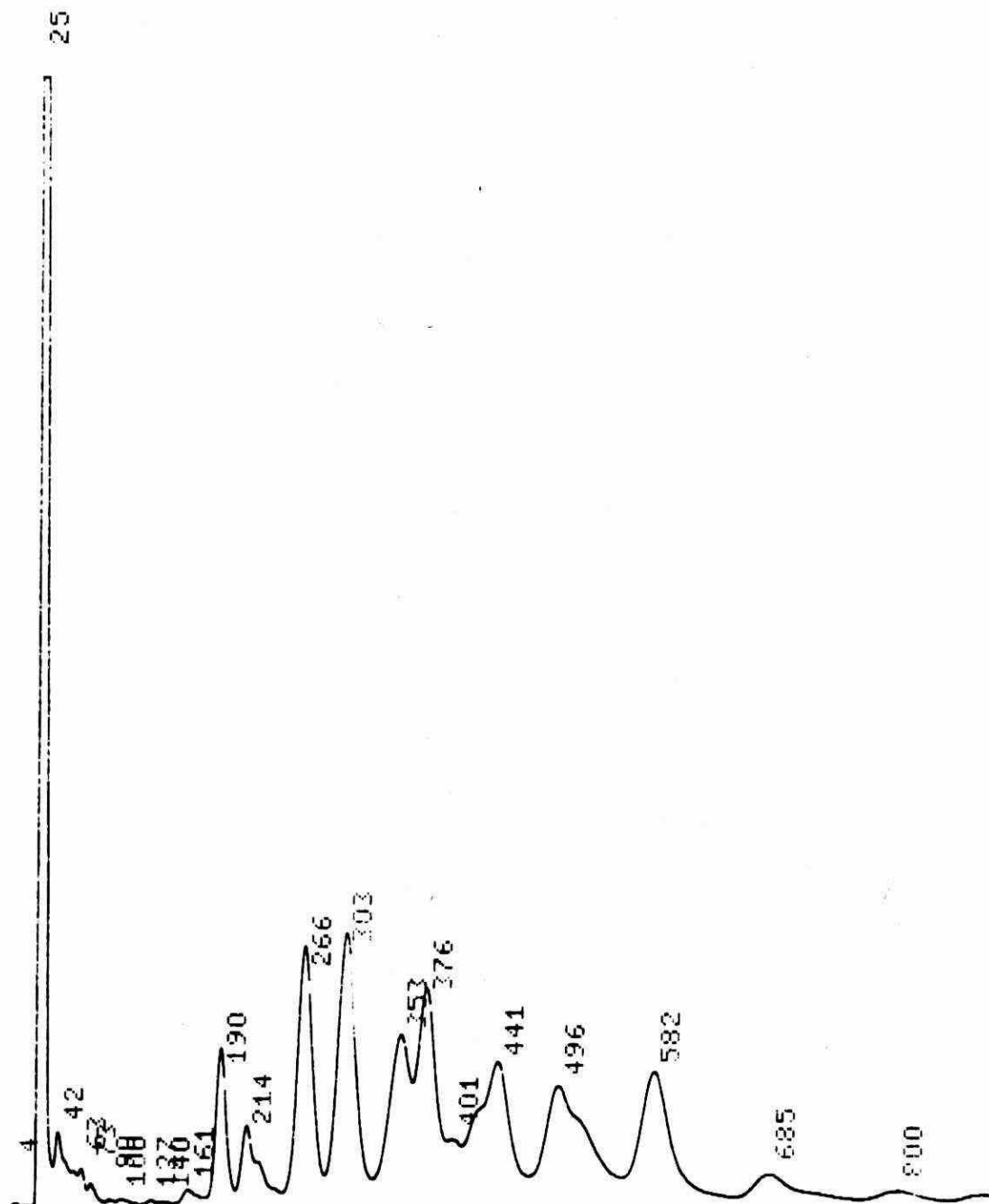
FIGURE 2.8 Chromatographic Profile of Standard Aroclor 1254 (0.1 μ g/ml)

FIGURE 2.9 Chromatographic Profile of Calibration Isomer Mixture

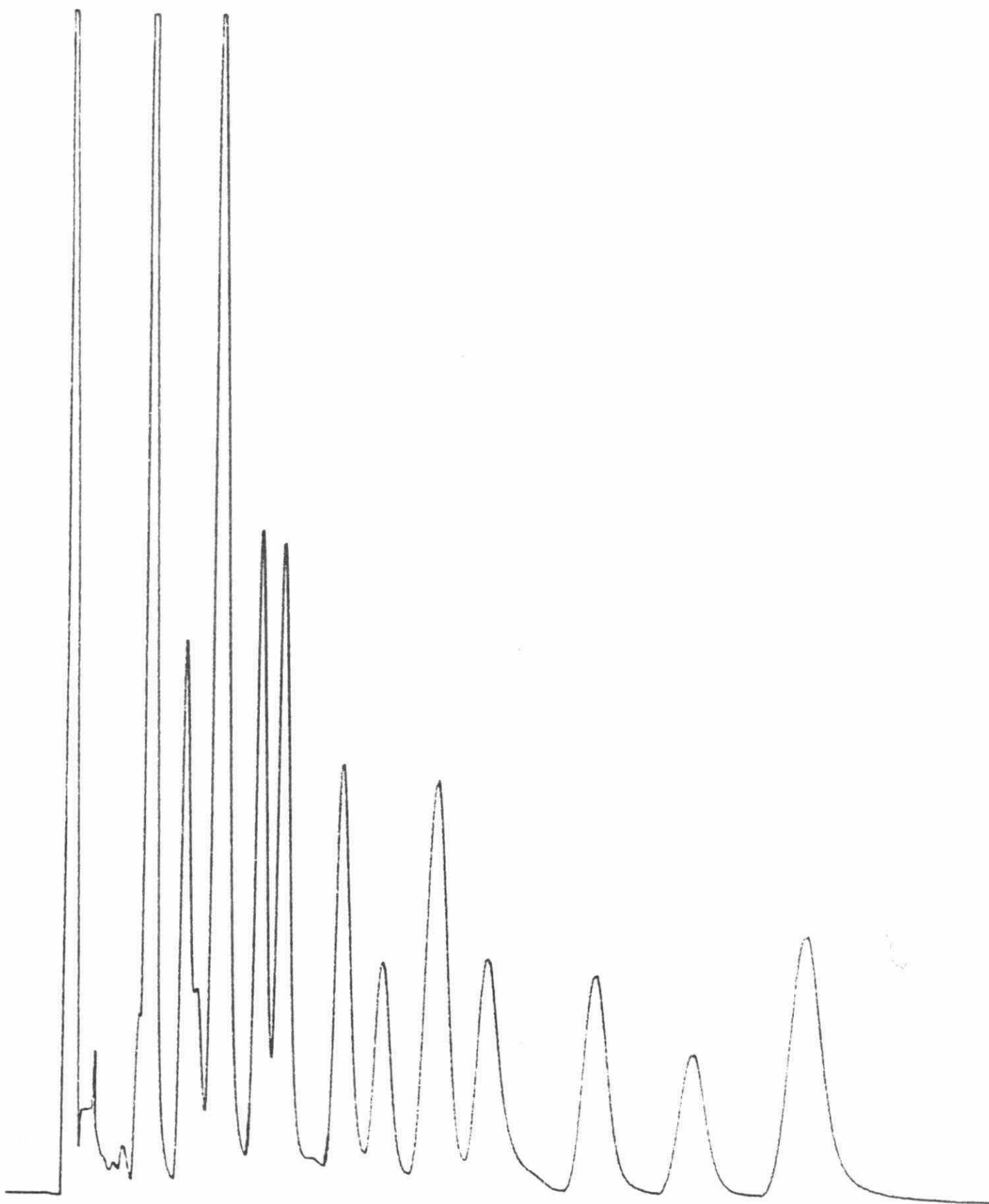


FIGURE 2.10 Chromatographic Profile of Blank Sample
(Computed total PCB = 0)

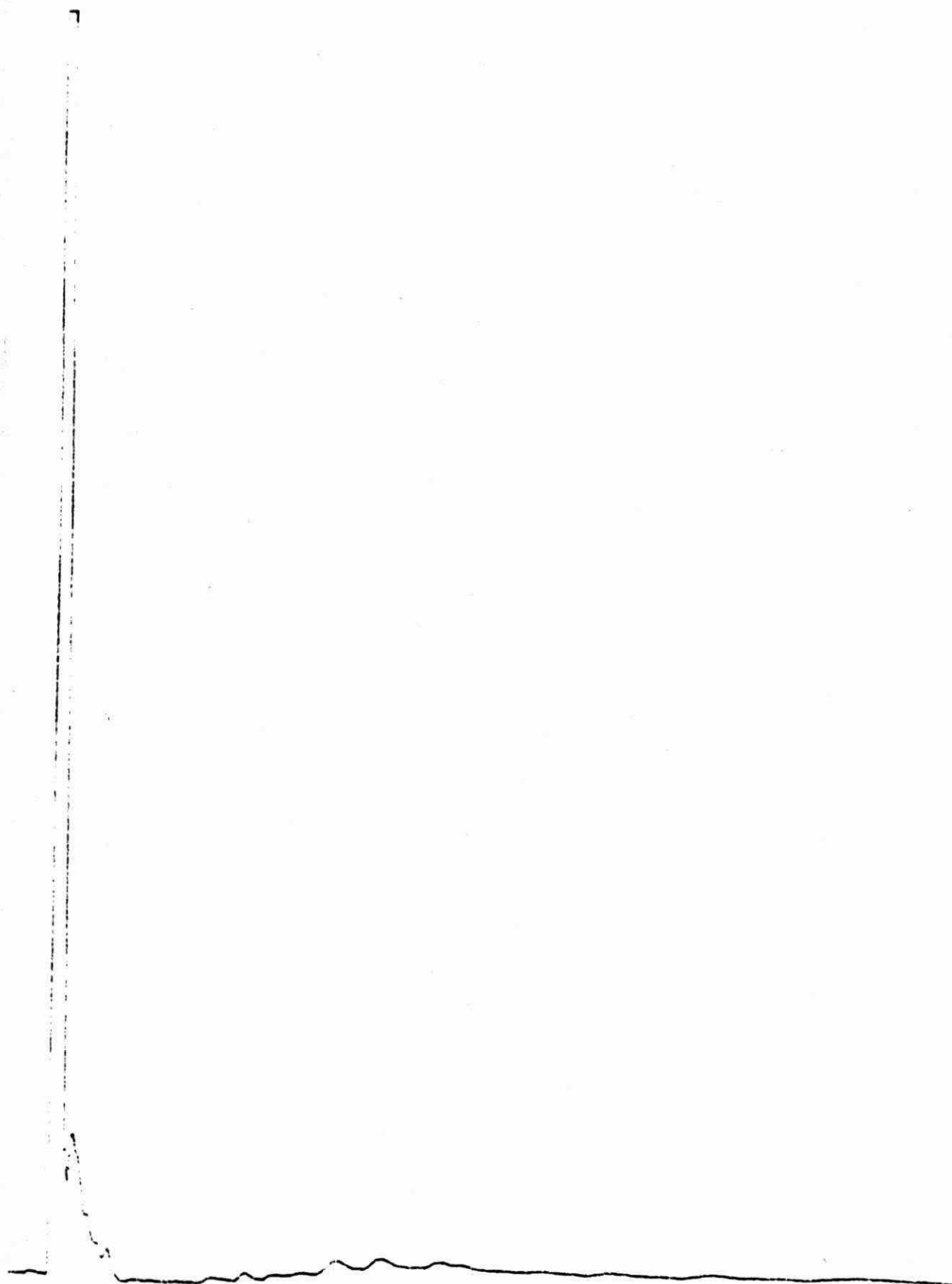


FIGURE 2.11

Chromatographic Profile of Blank Sample
(Computed Total PCB = 20ng)

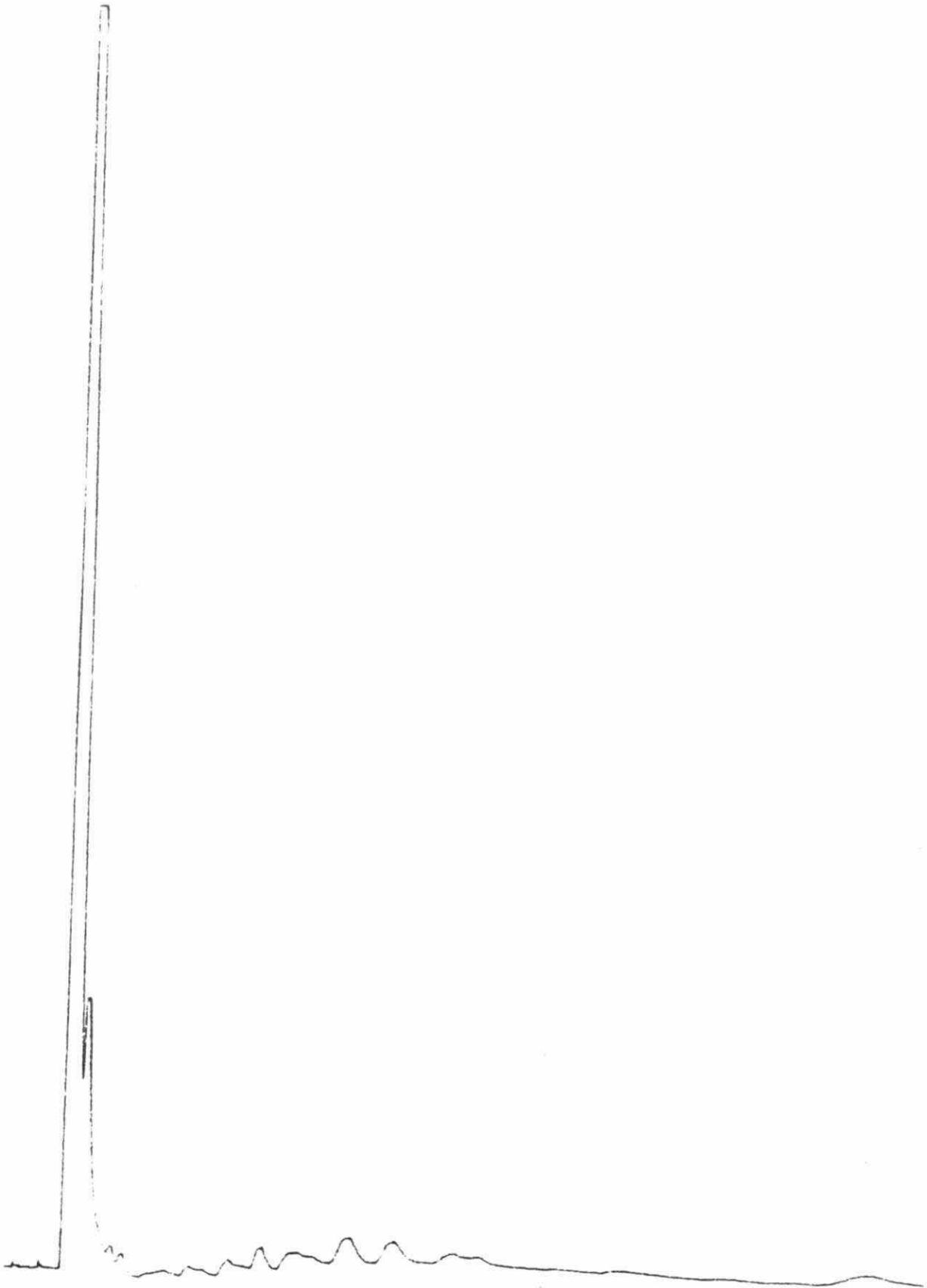


FIGURE 2.12 Chromatographic Profile of Sample from S1 Location
(Computed Total PCB - 269ng)

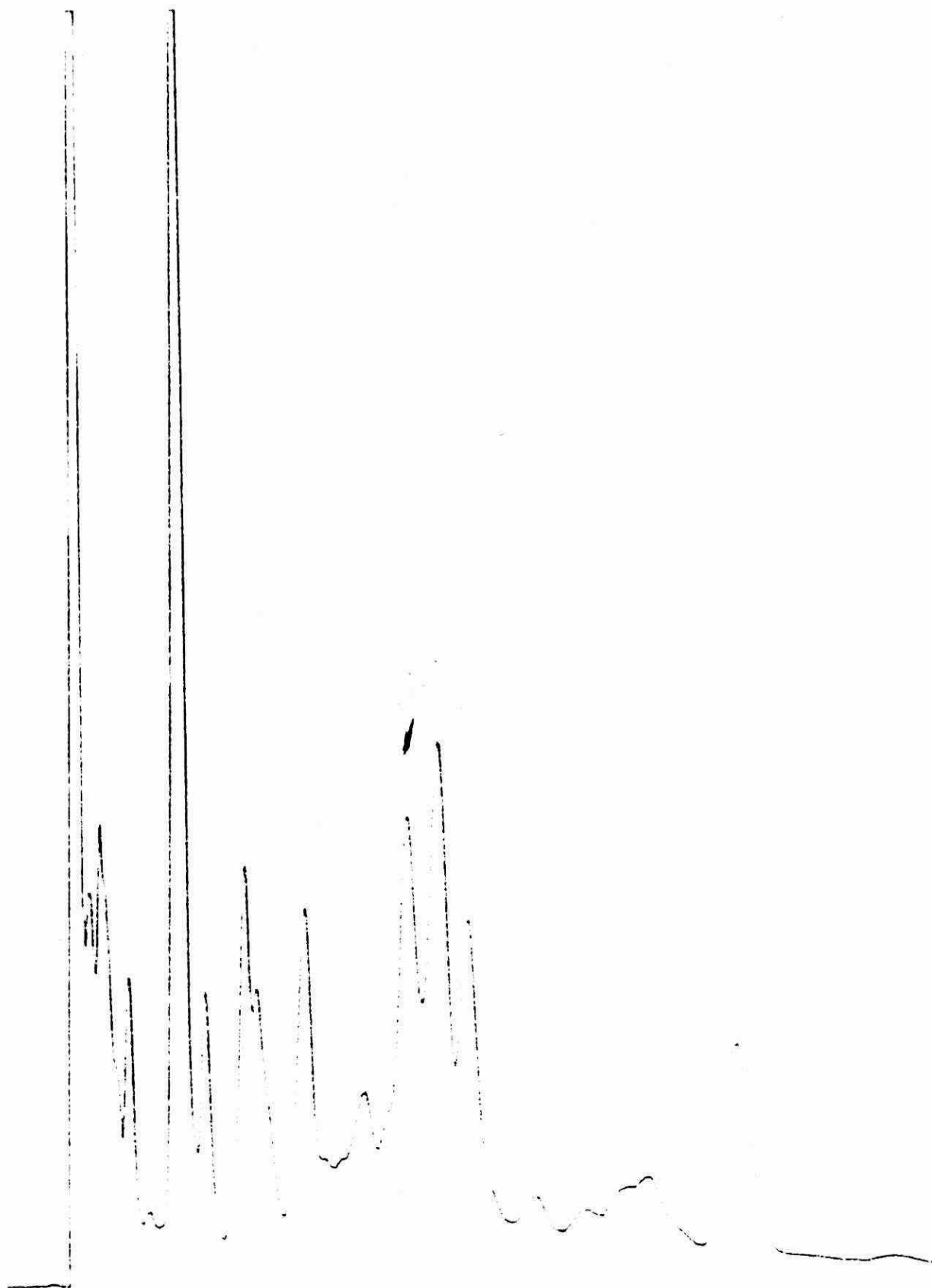


FIGURE 2.13

Chromatographic Profile of Sample from S2 Location
(Computed Total PCB = 259ng)

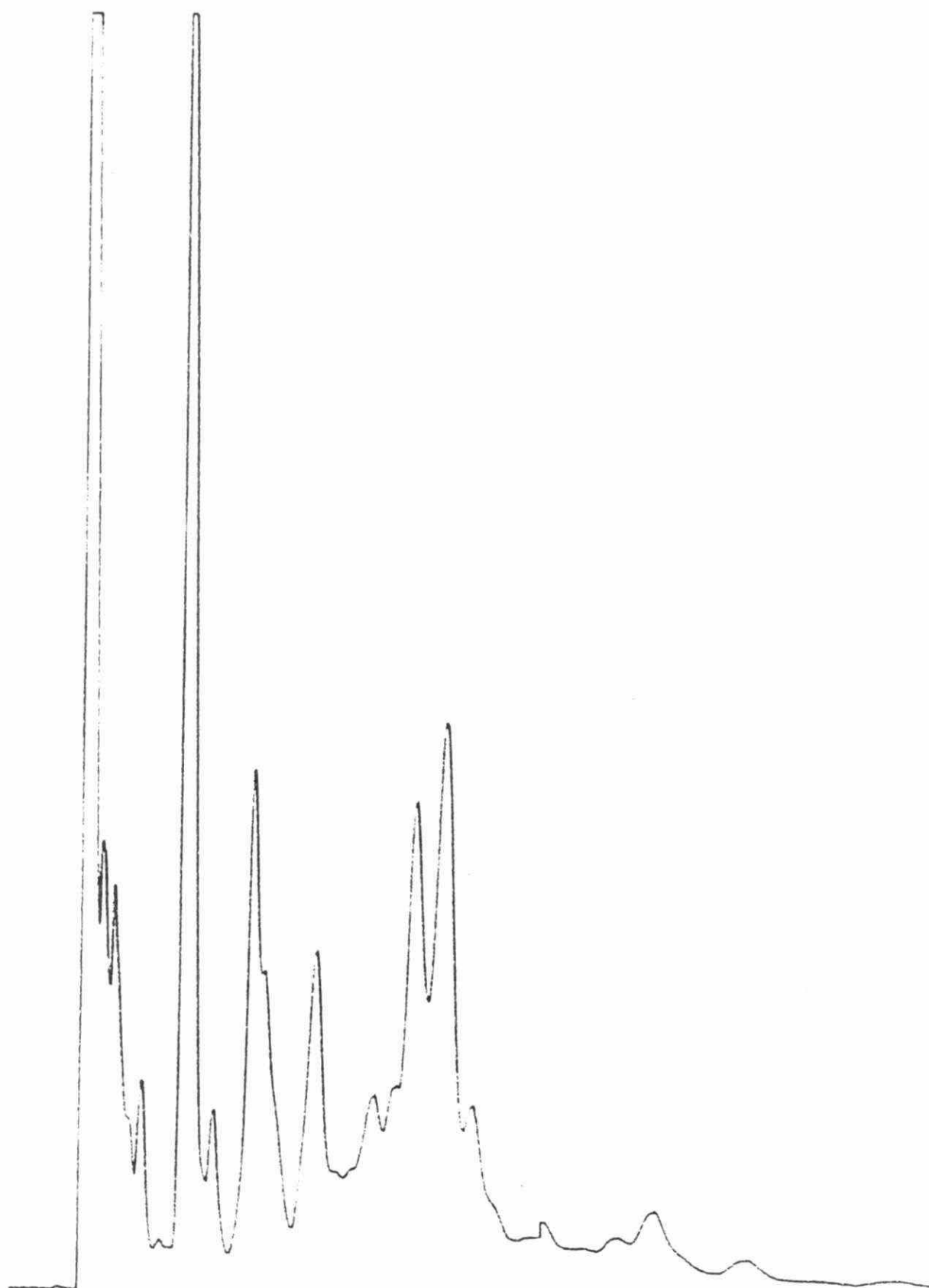


FIGURE 2.14

Chromatographic Profile of Sample from S3 Location

(Computed Total PCB = 134ng)

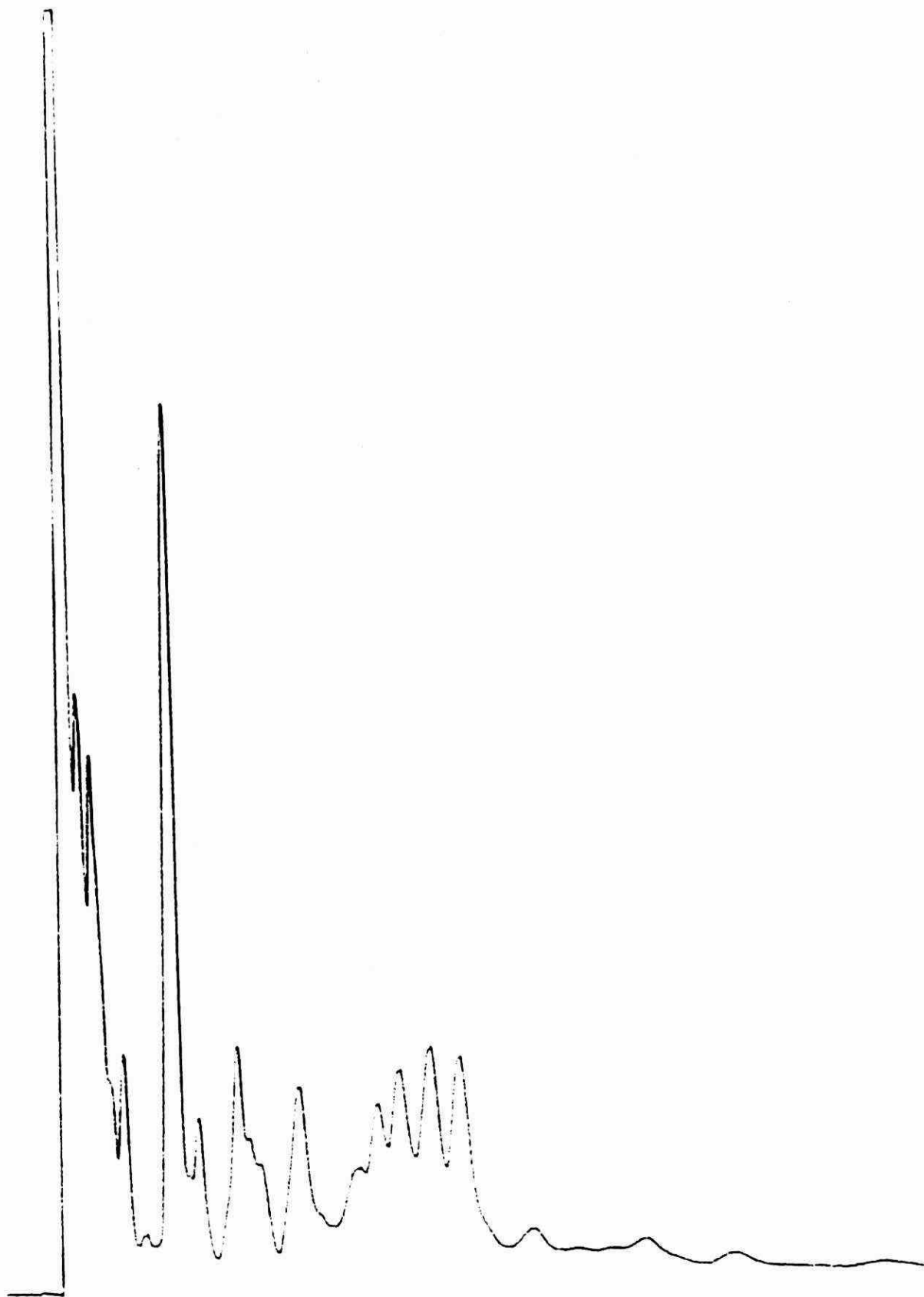


FIGURE 2.15

Chromatographic Profile of Sample from S4 Location
(Computed Total PCB = 66ng)

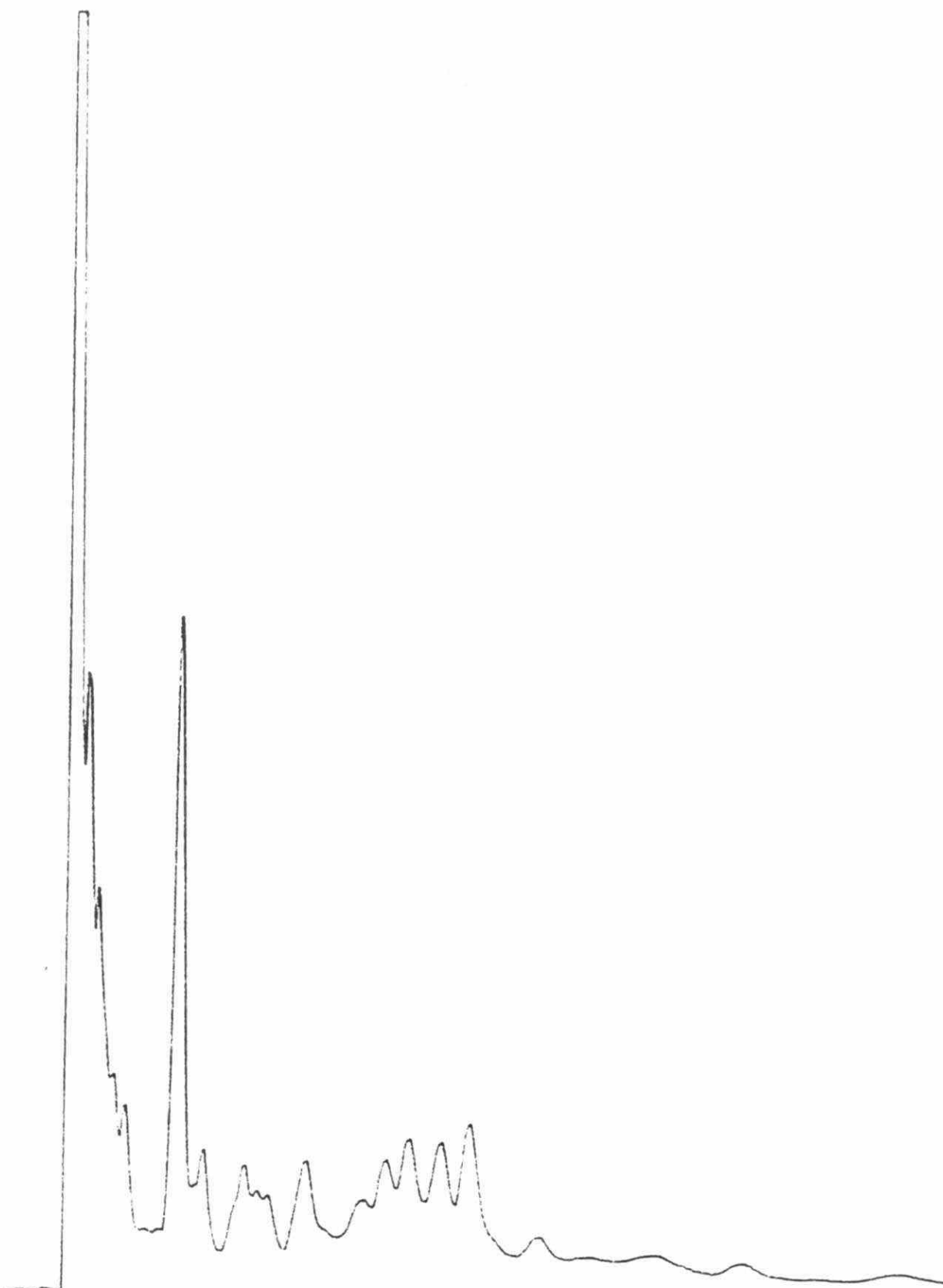


FIGURE 2.16

Chromatographic Profile of Sample from S5 Location
(Computed Total PCB = 179ng)

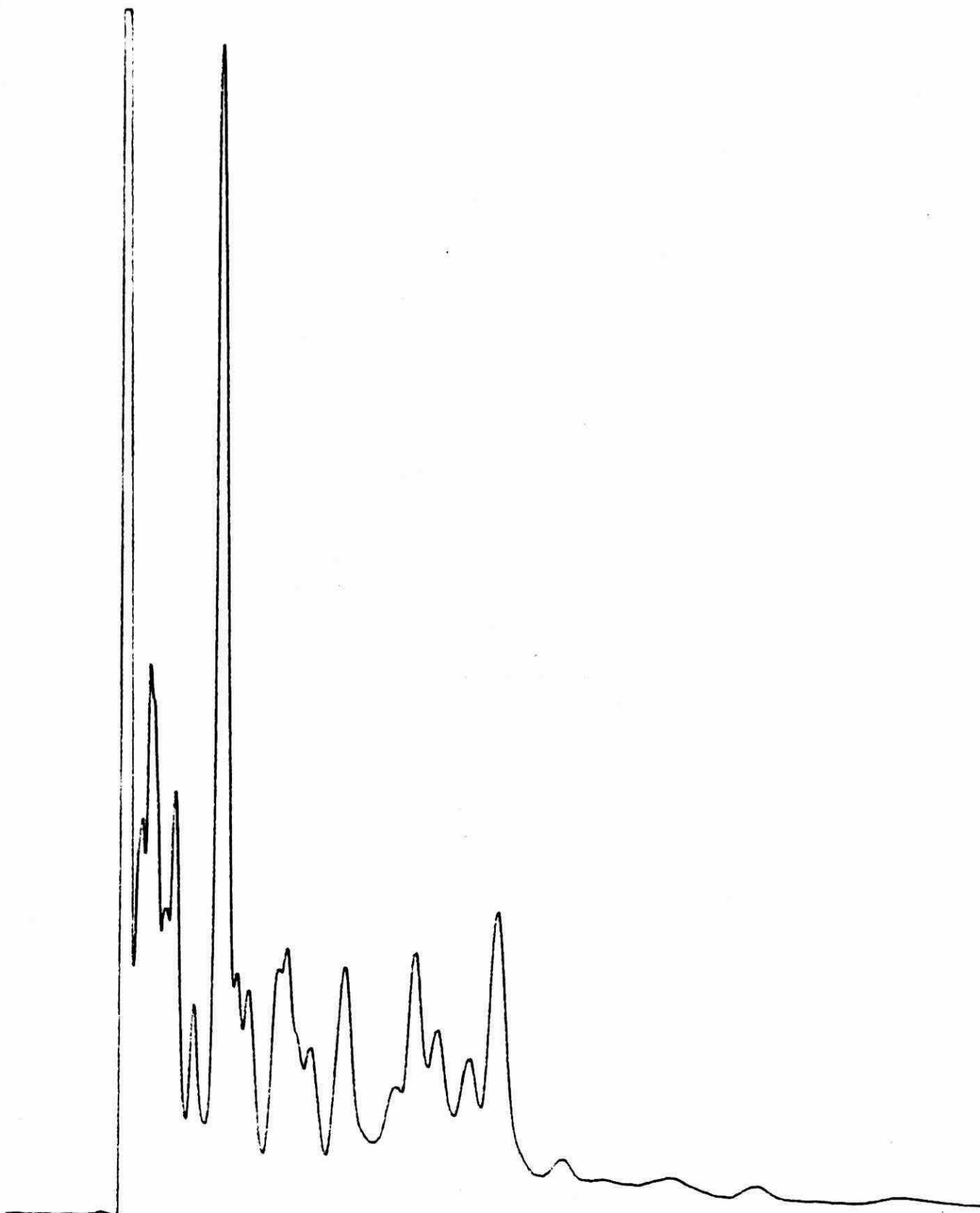


FIGURE 2.17 Chromatographic Profile of Sample From S6 Location
(Computed Total PCB = 800ng)

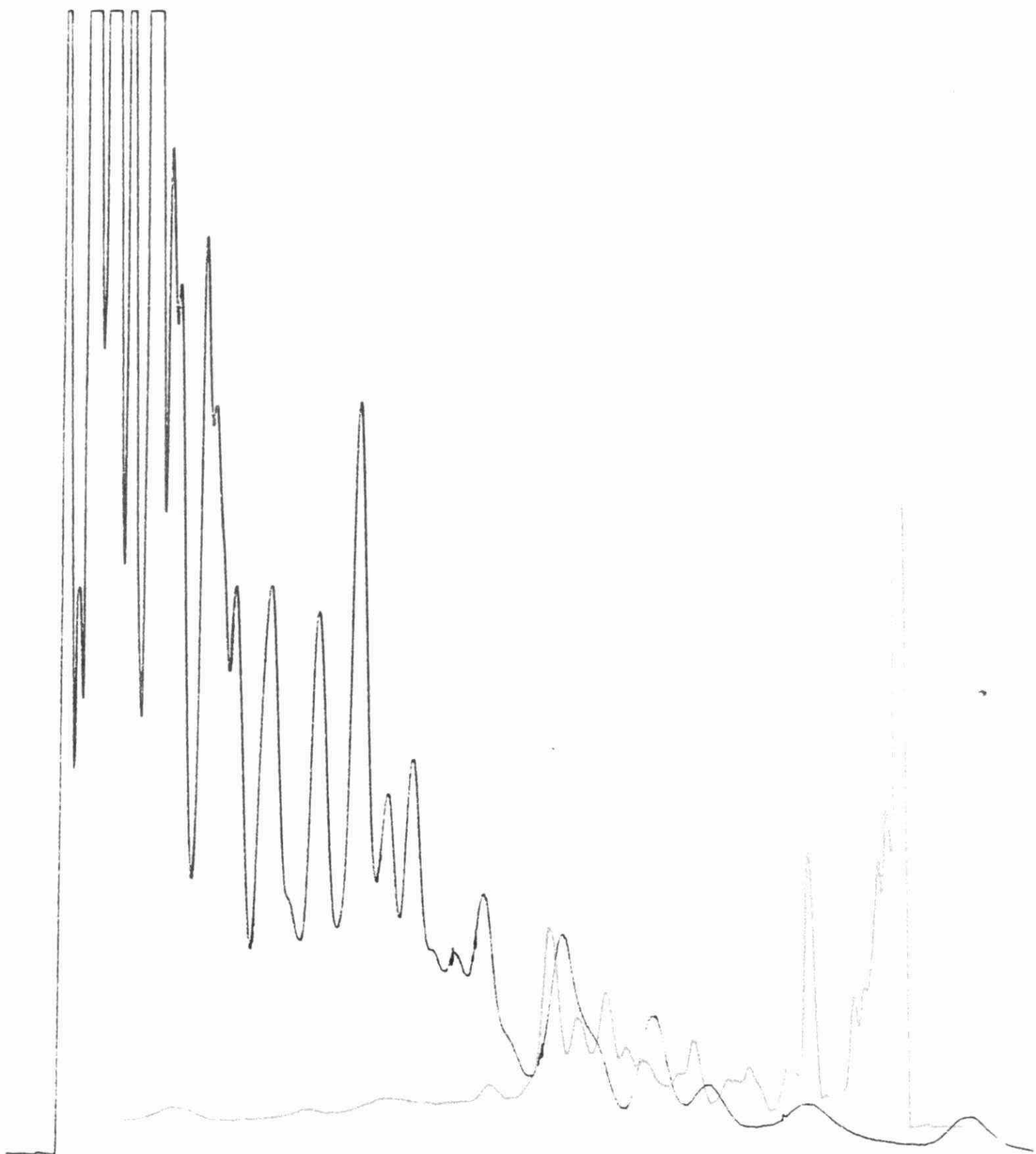


FIGURE 2.18 Chromatographic Profile of Sample From S7 Location
(Computed Total PCB = 101ng)

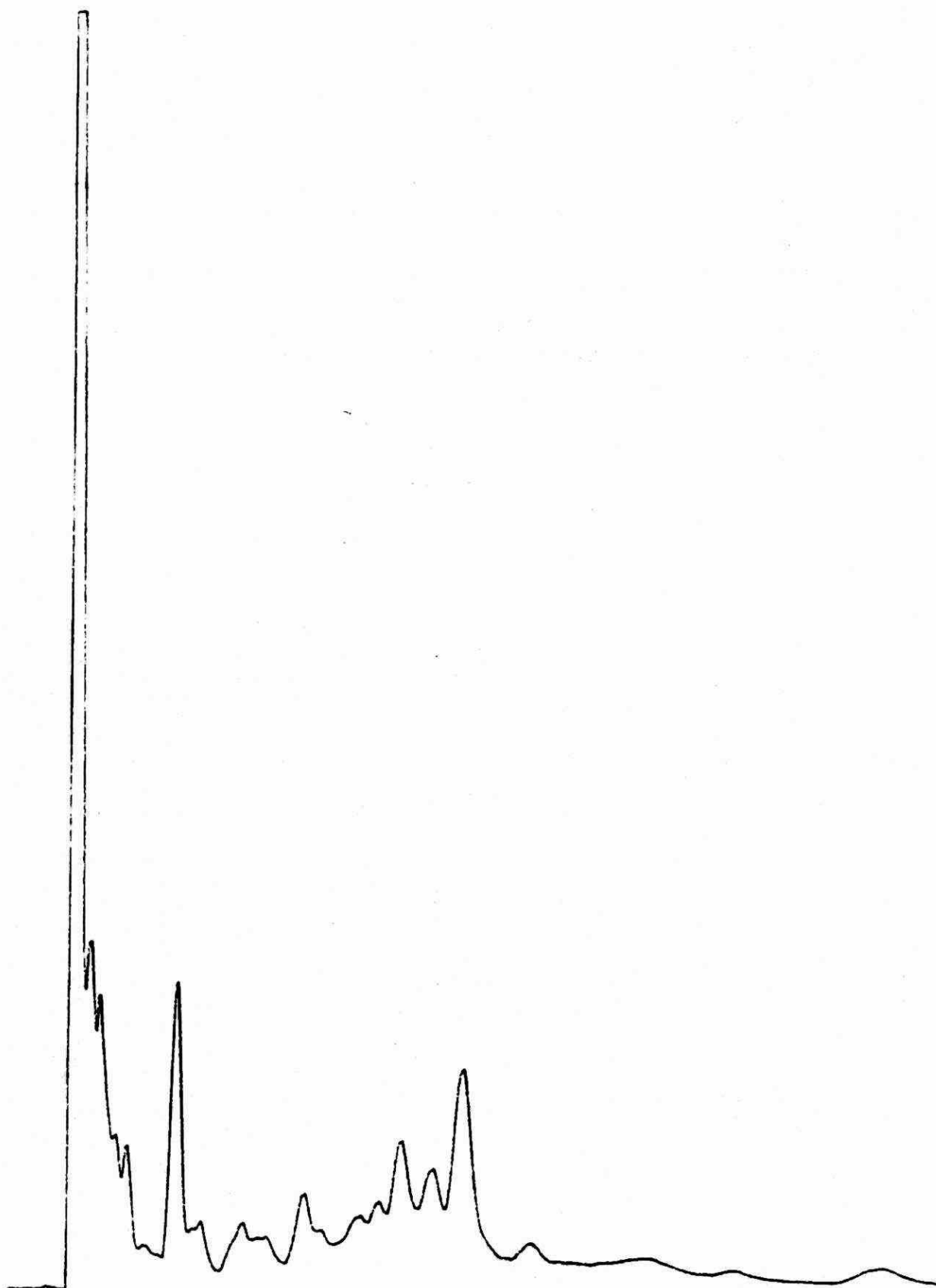


FIGURE 2.19 Chromatographic Profile of Sample From S8 Location
(Computed Total PCB = 135ng)

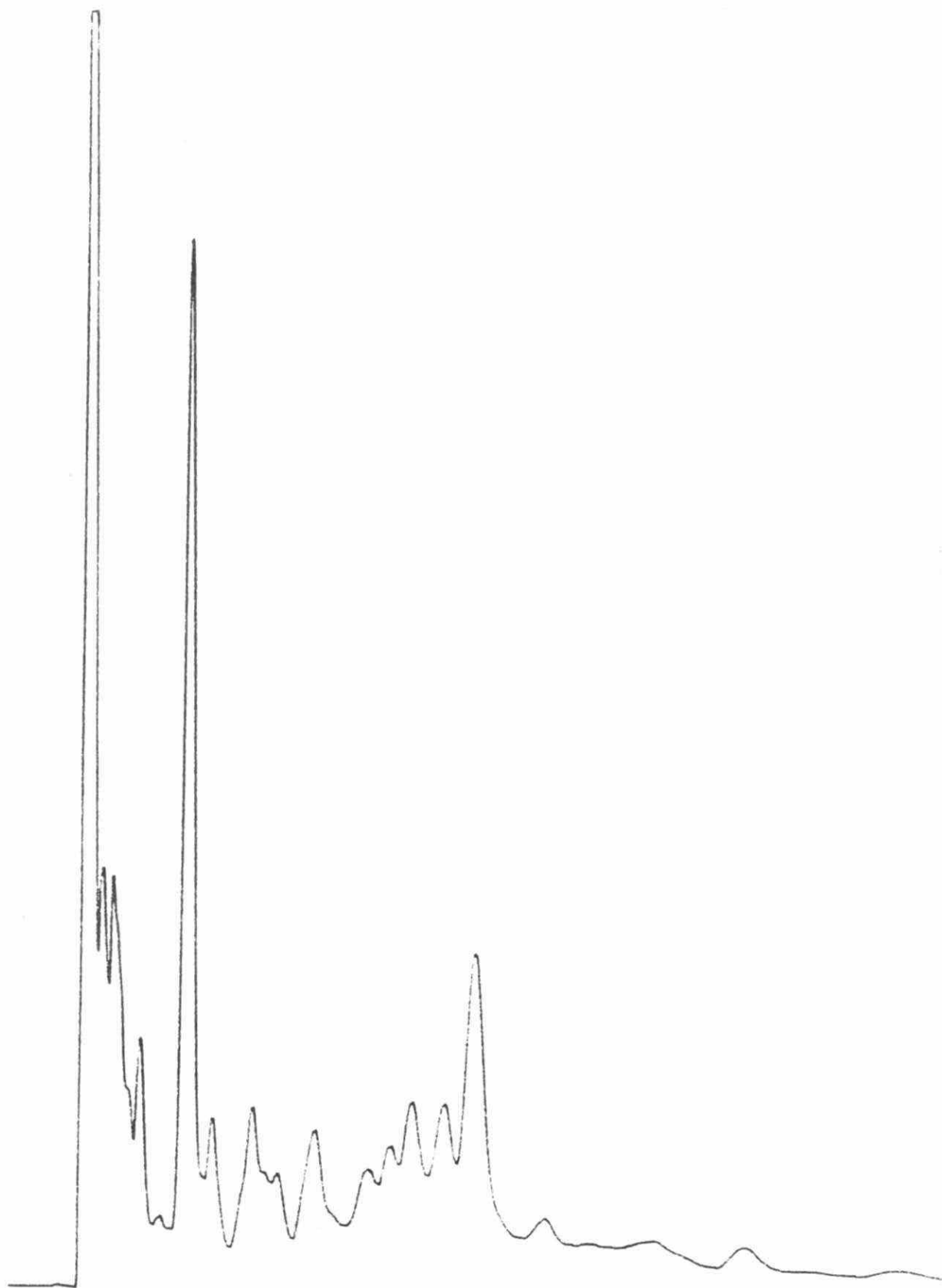


FIGURE 2.20 Chromatographic Profile of Sample From S9 Location
(Computed Total PCB = 228ng)

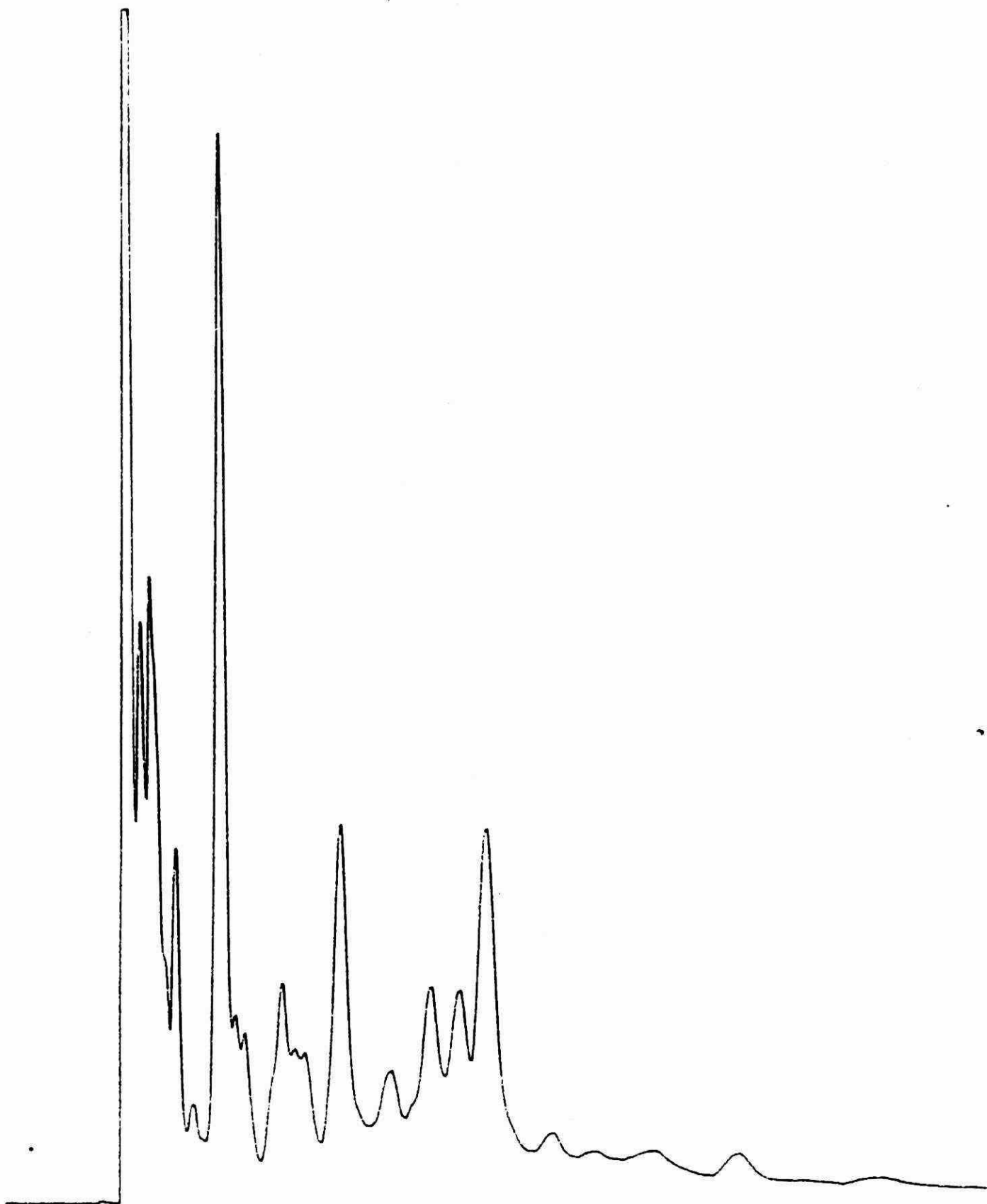


FIGURE 2.21

Chromatographic Profile of Sample From S10 Location

(Computed Total PCB = 235ng)

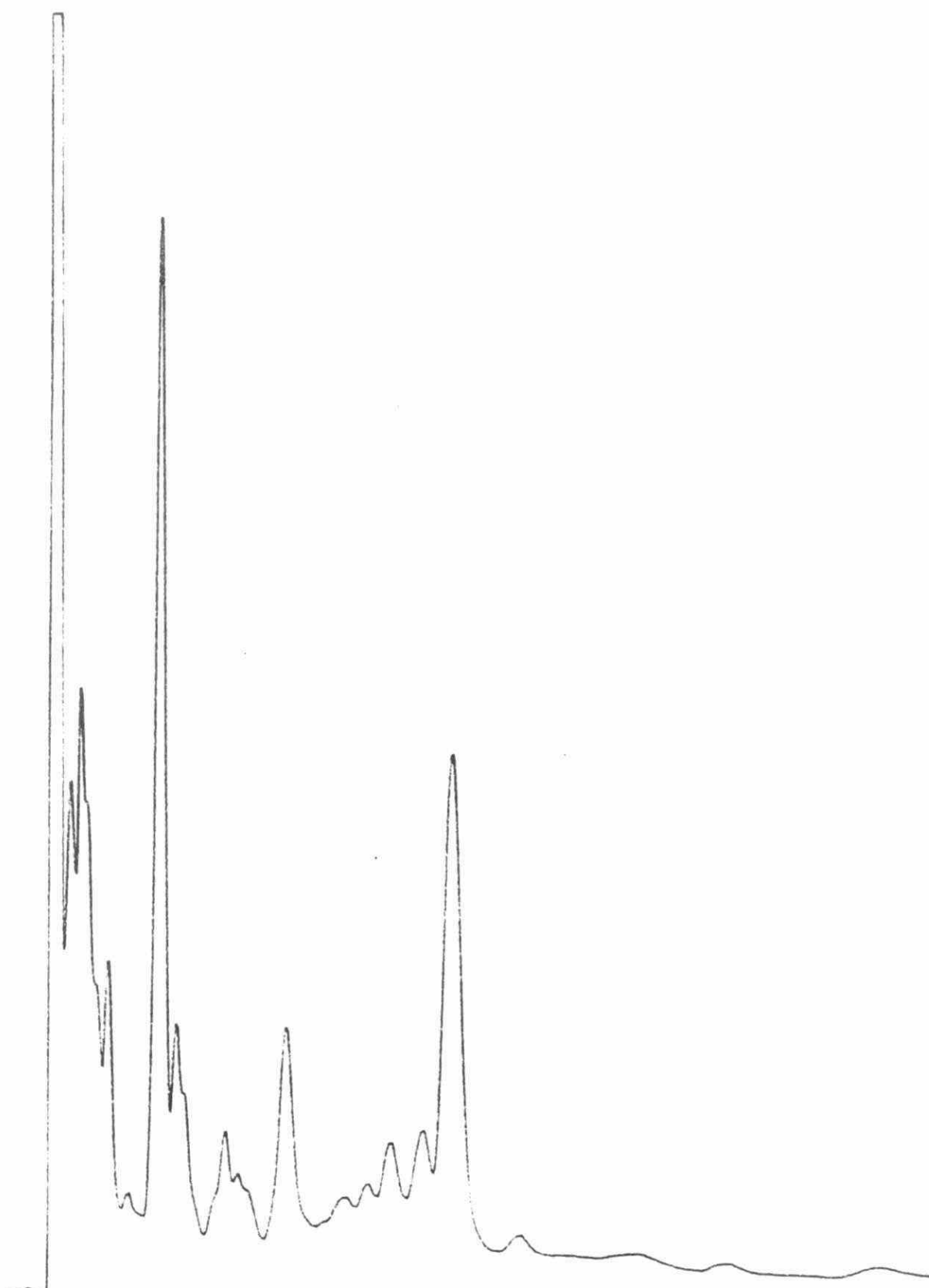
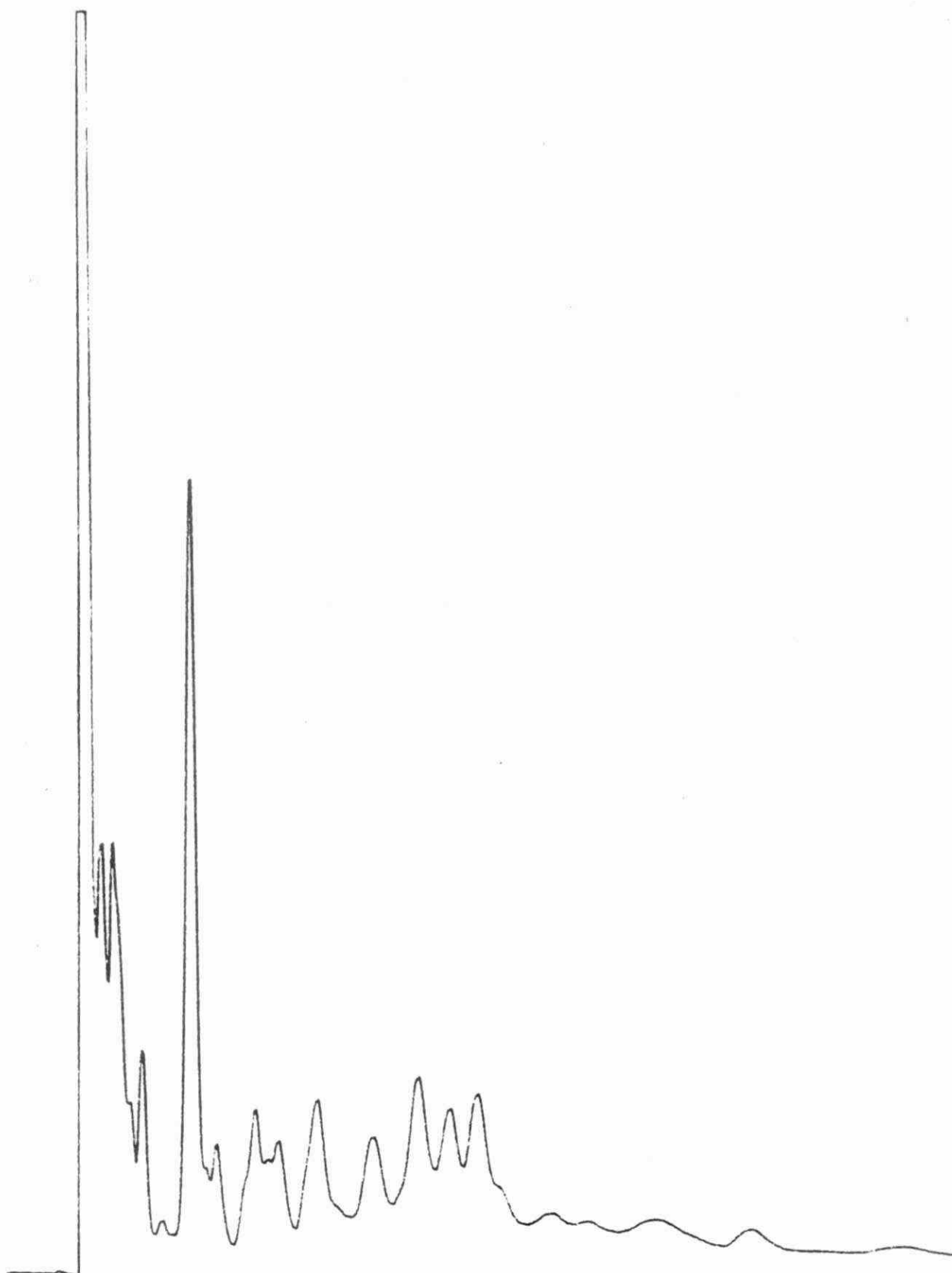


FIGURE 2.22

Chromatographic Profile of Sample From S11 Location

(Computed Total PCB = 107ng)



3. RESULTS AND DISCUSSION

3.1 PCB Concentrations for Blanks, Plant Property and Residential Air Samples

As described above, 24-hour average ambient PCB concentrations were measured for a period of 51 days at 11 stations located in the vicinity of the plants and throughout the residential areas northeast to northwest of the plants. The sampling sites were selected so as to define both fugitive and stack emissions from the plants and to provide data representative of the residential areas in which maximum ground level concentrations could be anticipated to occur. The results are shown in Table 3.1 together with blank determinations and explanatory notes regarding missing values. Initial evaluation of the monitoring results involved a general review of the validity of the data. On the basis of this review, 26 of the 612 determinations were rejected as invalid or of questionable significance. The footnotes to Table 3.1 give the reasons involved.

The procedure used to ensure low PCB levels in the Florisil tubes prior to exposure has been described in Section 2.3.2. In addition to this prescreening of each and every tube, one blank tube was processed each day of the survey. The blank tube was assembled, transported to and from the field, and stored prior to analysis in the same manner as the exposed tubes. The results of these blank analyses were expressed as "equivalent" concentrations assuming an average sampled volume of 14 m^3 . The overall average blank level was 1 ng.m^{-3} . The distribution of blank values was as follows:

Concn. Range (ng.m^{-3}):	<0.5	.51-.99	1.0-1.49	1.5-1.99	>2.0
Number of Values:	18	8	7	6	10
Standard Deviation:	0.9				

Thus, while the majority of the values were less than 2 ng.m^{-3} , a number of tubes were on occasion significantly higher. It was concluded that the best approach to using these blank determinations was to apply a single correction factor of 1 ng.m^{-3} to all samples. While there would at first appear to be some justification to apply the individual values to each daily set of results, it was the opinion of Ontario Research analysts that the observed variations in the blank levels were not primarily a consequence of the handling procedure, but rather, represented the variation

TABLE 3.1 CONCENTRATIONS OF TOTAL PCB ISOMERS (ng.m⁻³)A

Date	**	Indust. Station			Residential Stations								Comments			
	4	5	6	7	1	2	3	8	9	10	11	B	Approx % S-WSW Wind	Operating Data SLC	Tricil	Other
June 5/6	17	12	18	38	48	C	10	ND.	3	6	3	2.3	-	Normal	Normal	
6/7	5	5	18	3	22	C	6	4	8	ND.	8	2.6	38	"	"	
7/8	10	11	85	32	11	C	18	14	9	5	13	0.4	8	"	"	
8/9	5	8	4	9	9	C	7	ND.	3	5	4	0.2	0	"	Down	
9/10	ND.	3	18	16	3	C	27	ND.	ND.	4	7	2.4	0	"	"	
10/11	9	10	16	11	13	C	28	5	4	10	7	2.9	0	Down (#1)	"	
11/12	9	3	43	19	23	C	118 *	6	13	9	7	0.6	100	"	"	
12/13	5	9	22	5	7	C	27	6	3	4	3	0.3	33	"	Normal	
13/14	5	ND.	ND.	3	4	C	8	ND.	5	3	ND.	1.4	0	Down (#1,2)	"	
14/15	ND.	4	5	3	5	C	49	ND.	3	3	4	1.0	0	"	"	
15/16	12	6	21	14	8	C	10	21	7	ND.	9	0.2	38	"	"	
16/17	9	9	4	14	9	C	3	6	11	3	5	3.2	0	"	"	
17/18	33	13	23	11	14	C	42	4	6	5	5	0.2	46	"	Down	
18/19	7	17	ND.	ND.	14	C	19	5	10	5	4	0	0	"	"	
19/20	ND.	5	21	16	6	C	8	ND.	6	4	5	0.8	29	Down (#1)	Normal	
20/21	7	8	23	9	13	C	G	7	8	4	7	0.4	4	"	Variable	
21/22	4	4	11	8	7	C	19	ND.	5	6	11	2.1	0	"	"	
22/23	ND.	ND.	15	5	8	21	17	ND.	3	3	3	2.2	0	"	Down	S2 moved sampler
23/24	4	ND.	41	9	19	7	12	ND.	4	ND.	4	0.4	17	"	"	
24/25	D	7	36	5	19	9	10	24	7	4	9	0.6	33	"	"	
25/26	5	8	14	59	22	3	8	9	13	20	10	1.8	8	"	"	
26/27	37	28	46	7	39	24	77	8	16	12	8	0.1	38	Normal	"	
27/28	36	12	62	12	12	14	38	3	7	12	4	1.6	13	"	Normal	
28/29	14	11	17	7	9	6	27	11	6	11	4	0.7	8	"	"	
29/30	4	5	12	7	7	3	29	4	ND.	20	7	2.0	0	"	Down	
30/1	4	ND.	23	6	3	20	9	ND.	ND.	15	4	0.1	8	"	"	S3 moved sampler
July 1/2	ND.	ND.	12	4	3	5	4	3	ND.	24	ND.	0.2	38	Normal	Down	
2/3	ND.	ND.	11	19	ND.	4	ND.	3	ND.	3	6	0	0	"	"	
3/4	ND.	3	ND.	ND.	5	9	ND.	ND.	ND.	3	3	0.3	0	"	"	
4/5	35	9	20	19	6	10	22	9	5	22	5	0.7	8	"	"	

cont'd....

CONCENTRATIONS OF TOTAL PCB ISOMERS (ng.m⁻³)^A (Table 3.1 continued)

Date	**	Indust. Station				Residential Stations							Comments			
	4	5	6	7	1	2	3	8	9	10	11	B	Approx. % S-WSW Wind	Operating Data SLC Tricil		Other
July 5/6	22	9	44	16	13	16	13	13	10	18	11	0	33	Normal	Variable	
6/7	4	11	69	7	16	17	13	8	15	17	9	0	88	"	"	
7/8	4	14	59	G	13	12	8	9	8	6	9	1.4	4	"	Down	
8/9	6	3	34	4	8	5	4	4	6	4	7	1.1	21	"	"	
9/10	5	12	30	11	11	7	11	G	5	6	5	2.2	42	"	"	
10/11	3	5	10	3	6	5	4	3	ND.	4	6	1.5	0	"	"	
11/12	3	4	50	3	3	E	ND.	G	ND.	9	ND.	1.7	25	"	"	
12/13	5	13	146	11	9	6	6	ND.	7	9	5	2.4	42	"	"	
13/14	5	10	47	9	10	11	5	5	9	21	5	1.4	21	"	"	
14/15	11	9	68	11	5	6	9	ND.	11	12	6	1.4	17	"	"	
15/16	7	11	62	7	13	9	7	5	6	5	7	0.5	29	"	"	
16/17	ND.	4	41	7	7	7	35	4	3	22	5	F	21	"	"	
17/18	F	4	65	7	5	11	4	3	ND.	4	13	0.4	25	"	"	
18/19	6	13	75	9	12	16	7	6	10	6	11	F	67	"	"	
19/20	7	14	68	11	17	31	9	8	17	5	8	0.2	75	"	"	
20/21	4	25	71	10	5	14	6	6	8	8	15	1.6	50	Down (#1,2)	"	
21/22	27	24	57	18	15	40	11	5	22	15	10	0.8	29	Normal	"	
22/23	10	17	91	25	29	33	12	13	13	10	12	0.9	75	"	"	
23/24	4	4	12	11	7	13	6	6	4	13	5	1.0	4	"	"	
24/25	23	5	42	12	8	12	5	6	5	17	11	0.4	0	"	"	
25/26	53	30	40	50	10	20	13	11	14	16	11	1.8	54	"	"	

* Suspected local interference.

Kilns Down

** Station located adjacent to industrial property.

A - Results after subtracting the average blank value of 1 ng.m⁻³ (see note B)

B - Equivalent concentration of the unexposed blank collector tubes which were transported along with the sample tubes. The results based on passage of an equivalent quantity of air (approximately 14 m⁻³).

C - Data rejected on the basis of a probable local interference on site.

D - Result rejected on the basis of suspected sample contamination.

E - Sample tube broken.

F - Data rejected as sample tubes were used before adequate precleaning.

G - No value due to lost field record

ND.- Not detectable.

in residual PCB levels in the extracted Florisil material (see Section 2.3.2).

On the basis of the sensitivity of the analytical method determined with standard samples, and the volume sampled ($10\text{--}15\text{m}^3$) by the Nutech samplers over a 24-hour period, the estimated theoretical detection limit of the method was $1\text{ ng}\cdot\text{m}^{-3}$ or less, in accordance with the specifications for the study (5). However, because of the persistence of trace amounts of PCBs (or interfering materials) on the sample tubes despite the thorough cleaning procedure used, it was necessary to define a practical detection limit in terms of the blank determinations summarized above. In accordance with normal statistical procedures (9), the practical detection limit was defined as the average blank value plus twice the standard deviation, resulting in a value of $2.83\text{ ng}\cdot\text{m}^{-3}$. Thus, all values less than or equal to $3\text{ ng}\cdot\text{m}^{-3}$ were considered to be less than the detection limit of the method and were treated as zero in all subsequent evaluations of the data.

A number of approaches have been used in evaluating the data, including:

- a general assessment of the measured levels at each site,
- directional distributions have been calculated,
- average isomeric patterns have been determined at each site.

The sampling sites located on or directly adjacent to the company properties (S4, S5, S6, S7) and in the residential areas (S1, S2, S3, S8, S9, S10, S11) are shown in Figure 2.1. Average concentration ranges, standard deviations and values exceeding limits of 10 and $20\text{ ng}\cdot\text{m}^{-3}$ are summarized for both sets of data in Table 3.2.

The plant property sites (S4, S5, S6, S7) can be assumed to reflect direct contributions from the industrial operations with fugitive emissions from storage and handling being more important than stack emissions at

TABLE 3.2 SUMMARY OF AMBIENT AIR PCB CONCENTRATIONS

	**	Industrial Property			Residential Stations						
	4	5	6	7	1	2	3	8	9	10	11
No. of Samples	48	50	51	50	50	33	50	49	50	51	51
Arithmetic Mean (ng.m ⁻³)	10	9	36	12	12	13	17	6	7	9	7
Standard Deviation (ng.m ⁻³)	12	7	29	11	9	9	20	5	5	7	3
Range (ng.m ⁻³)	ND.-53	ND.-30	ND.-146	ND.-59	ND.-48	3-40	ND.-118	ND.-24	ND.-22	ND.-24	ND.-15
¹ Number of Days that Concentrations Exceeded 20 ng.m ⁻³	8	4	32	5	6	7	12	2	1	6	0
¹ Number of Days that Concentrations Exceeded 10 ng.m ⁻³	12	18	44	23	22	17	23	7	10	17	9

¹ No criteria have been established, the values of 10 and 20 ng.m⁻³ were used for comparative purposes only.

ND = < 3 ng.m⁻³

** Station located adjacent to industrial property.

these sites.

Average concentrations ranged from 9 ng.m^{-3} on the St. Lawrence property to 36 ng.m^{-3} at the northeasterly boundary of the Tricil property (S6). The highest individual level (146 ng.m^{-3}) observed during the survey occurred at this site, but levels at this location otherwise generally did not exceed 85 ng.m^{-3} . Standard deviation values for these 4 sites (Table 3.2) show a comparable distribution of values about the mean at each site.

No ambient air quality criterion has yet been promulgated for PCBs in Ontario. For the purposes of this study, 10 and 20 ng.m^{-3} have been selected as arbitrary references with which to compare the observed values. Individual results at the plant property sites were found to exceed 20 ng.m^{-3} about 25% of the time, with exceedences occurring most frequently adjacent to the Tricil plant (S6). Levels in excess of 10 ng.m^{-3} occurred ~50% of the time, with the frequency of occurrence considerably higher at S6 than at the other sites.

As mentioned above, fugitive rather than stack emissions are likely to be the major sources of PCB levels at these sites. The location of storage facilities for waste solvents in relation to sampling points at both companies are shown in Figure 3.1. At St. Lawrence Cement the sample point was located about 1,350 ft. from the truck discharge point and the waste solvent storage tanks. The sampler at Tricil was positioned about 700 ft. from both the truck discharge and storage tanks and 200 ft. from a number of 45 gallon storage barrels. The major components of the PCB concentration/wind direction correlations (described later) tend to indicate these facilities at both companies as sources of PCBs.

It should be noted that both samplers on Tricil property were positioned near the ground (S6, S7) whereas the samplers near and on St. Lawrence Cement property (S4, S5) were located on rooftops. Thus, results at Tricil may tend to be more influenced by any previous nearby spills.

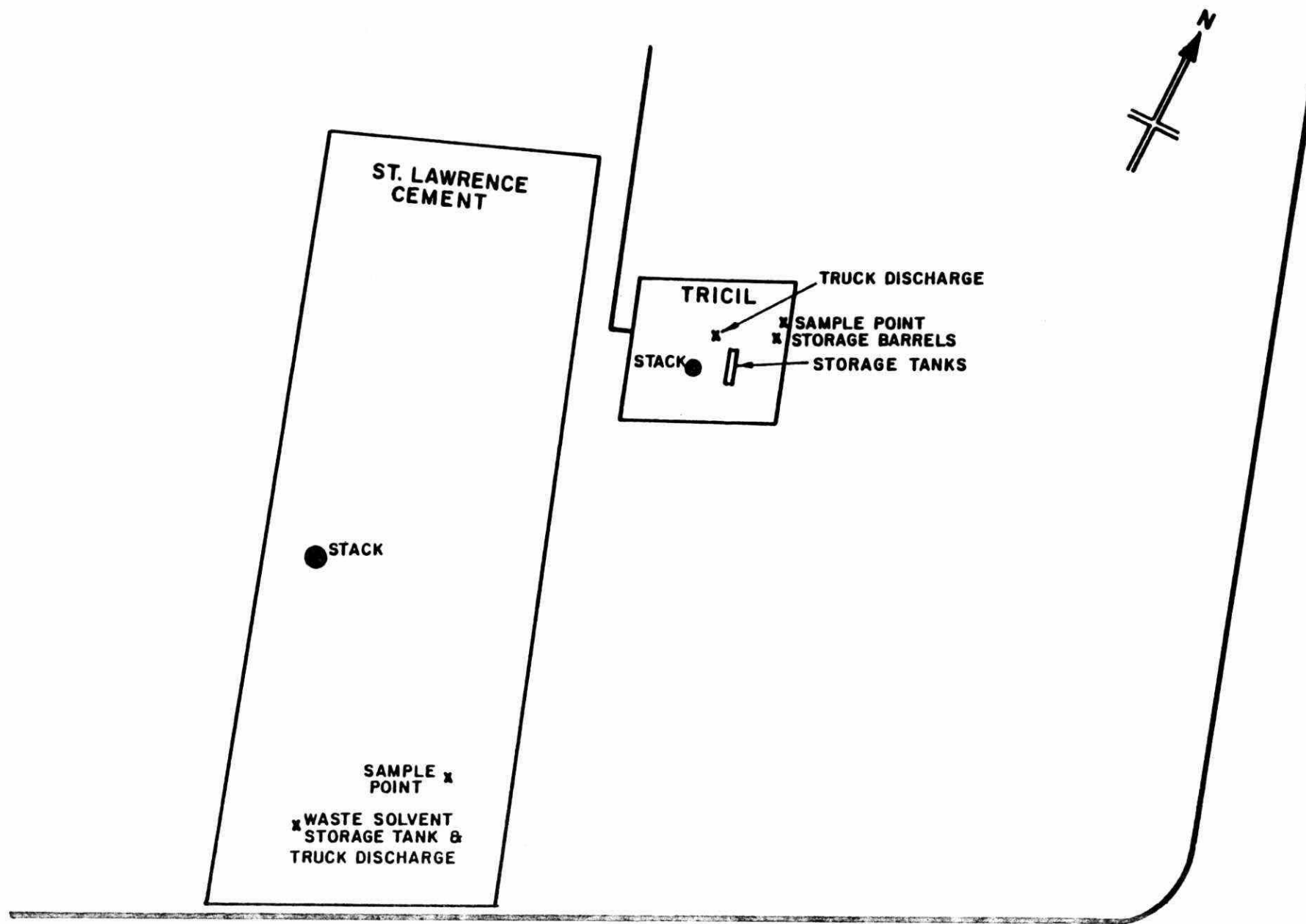


FIGURE 3.1 Waste Solvent Handling and Storage Areas at St. Lawrence Cement and Tricil

Shutdown of the Tricil plant incinerator on or about July 11, 1978, provided an opportunity to directly assess the importance of incineration relative to accumulated contamination and handling losses at the plant site. Inspection of the daily average values at the adjacent sites (S6 and S7) shows no significant reduction in levels following the shutdown. Indeed, at S6 average levels following the shutdown were higher than during operation, without including the anomalously high value which occurred on July 12/13, 1978. Thus, it must be included that factors other than incineration activities were predominant in determining ambient PCB levels at these plant property sites, and losses from contaminated storage and handling areas on the plant property appear as the most probable source.

The St. Lawrence Cement plant also was shut down for approximately 2 weeks in June (Table 3.1). Average levels at S4 ($\sim 8 \text{ ng.m}^{-3}$) and S5 ($\sim 7 \text{ ng.m}^{-3}$) were only slightly less than the average for the entire survey period suggesting that direct losses during transfer operations are less important than accumulated contamination of the handling area.

Residential sampling locations were chosen to represent typical PCB levels in the areas in which any emissions from St. Lawrence or Tricil would most likely make a significant contribution to ambient levels. Average concentrations at these stations ranged from 6 ng.m^{-3} to 17 ng.m^{-3} . As discussed later, the second highest value which occurred during the entire survey period (118 ng.m^{-3}) was measured at S3 during a period when local interferences were suspected. If such interferences are excluded, it appears that typical maximum values in the residential area ranged from $15\text{--}48 \text{ ng.m}^{-3}$ during the test period. It must be emphasized that these are upper limits to prevailing PCB concentrations because of the possibility of positive interferences by compounds with similar retention times (Section 2.3.4) and this will be discussed in further detail later in the report.

With the exception of S6 there is not as great a difference between on property fence-line and residential sites as anticipated. For example, S1, S2 and S3 located in the more remote residential areas, all show levels comparable

to S7 which is located between St. Lawrence Cement and Tricil. Similarly, the "upwind" site (S4) shows levels not significantly different from other locations. The difficulties experienced with suspected local interferences at S2 should be noted. During the early part of the survey high results were obtained, and after relocation of the sampler because of neighbour complaints of interference with television reception, levels decreased quite significantly, indicating a very local source of contamination.

A similar effect, but to a lesser extent, was suspected at S3, but it did not prove possible to correlate known activities with abnormal levels and so these suspect data are included in the average value of 17 ng.m^{-3} for this site. A number of other features of the data suggest that some local effect contributed to the higher than average levels at this site:

- high levels tended to occur in conjunction with northwesterly winds (not generally found at other stations)
- measured levels decreased substantially after the monitor location was changed 50 feet to the north because of a noise complaint from neighbours.

Thus, if allowance is made for these suspected interferences, average concentrations at the residential sites ranged from $6 - 12 \text{ ng.m}^{-3}$ and are consistent with the limited data from earlier studies (1,3,4). In making any detailed comparison of concentrations obtained in this and earlier studies, the ongoing modifications being made to calibration procedures must be taken into account and the subjective nature of currently used methods recognized (4).

As summarized in Table 3.2, values in excess of 20 ng.m^{-3} occurred approximately 4 times (less than 10%) at each of the residential sites and thus were significantly less frequent than at the plant property sites. Values in excess of 10 ng.m^{-3} at the residential site accounted, on average, for ~31% of the samples collected. Standard deviations for these sites, with the exception of S3, showed a somewhat narrower distribution of values than at the industrial fence-line sites. The main features of the distribution of values at both the on property and residential sites can be summarized as follows:

- the pattern from station to station generally concurs with the average concentrations, with very high levels occurring most frequently at S6, on the Tricil plant. Similarly, S3 shows values which are believed to reflect local interferences
- exceedences of 20 ng.m^{-3} occurred, on average, approximately 4 times at each of the residential sites during the course of the survey
- exceedences of 10 ng.m^{-3} at the residential sites were much more frequent, ranging from 7-23 for the individual locations.
- prevailing winds associated with values $>20 \text{ ng.m}^{-3}$ generally confirmed the directional correlations calculated by other methods (see below) and provided further evidence of the existence of anomalous effects at S3
- there was no tendency for widespread "fumigations" or "episodes" to occur. That is, high values did not tend to occur concurrently. On only 5 days did more than 4 values $>20 \text{ ng.m}^{-3}$ occur and the maximum number of concurrent values exceeding 20 ng.m^{-3} on any one day was 6 (Day 22)
- values $>20 \text{ ng.m}^{-3}$ were quite evenly distributed throughout the survey period.

The ambient data also have been evaluated in terms of plant operation. As discussed briefly above, the Tricil incinerator was shut down on or about July 11, 1978, providing an opportunity to assess the importance of incineration relative to storage and handling activities. Results obtained at S2, S6 and S9 were evaluated to determine if any significant reduction in PCB levels occurred subsequent to closure of the incinerator. Initially, average levels at these sites were calculated for "operating" and "not operating" days, using only those days when SW winds prevailed for at least 20% of the time. Data for the entire survey period was used. Relatively few days of operation under these conditions occurred (6 days at S6, 5 days at S9 and 2 days at S2). Comparison of these days with the more frequent days of shutdown conditions showed no significant reduction in PCB levels at these sites. Indeed, these selected results suggested that higher levels occurred during shutdown periods.

Average concentrations for the entire periods before and after the Tricil shutdown also were calculated, omitting the anomalous value of 146 ng.m^{-3} at S6 for July 12/13. The results were:

	<u>S2</u>	<u>S6</u>	<u>S9</u>
Concentration before, ng.m^{-3}	10	25	6
Concentration after, ng.m^{-3}	17	57	9

Thus, it must be concluded that factors other than current emissions from the Tricil incinerator were predominant in determining these ambient PCB levels during the survey period.

3.2 Correlation of PCB Concentrations with Meteorological Conditions

Wind direction and velocity measurements were made at the 12m level at the MOE sewage treatment facility approximately 450 m. to the southeast of the Tricil property (Figure 3.3). These data have been used in conjunction with the PCB measurements to determine if predominant PCB sources could be identified. The extremely low levels of PCBs being measured required that 24-hour sampling periods be used to ensure a sufficiently large sample for analysis. It is not practical to quantitatively define a prevailing wind condition for such long periods and so statistical methods must be used. A technique used by Samson et al (7) and others (8) has been employed to determine if any statistically significant correlation exists between the observed PCB levels and meteorological factors such as wind direction and speed. In this approach, a frequency distribution of the parameter of interest (wind direction, for example) is calculated for each 24-hour sampling period. Then, a least squares correlation between the pollutant concentration and the number of hours of wind for each direction on each day is calculated. The resulting correlation coefficients provide an indication of the tendency of pollutant concentrations at a given site to be associated with a given wind direction.

The results of the PCB concentration/wind direction correlations are presented in Table 3.3. In Figure 3.2, the correlation coefficients are presented as trend charts for each station. In these plots, positive values indicate a positive correlation of PCB concentration with wind direction. With the exception of S7 (west of Tricil), all stations show a general trend to positive

TABLE 3.3 CORRELATION COEFFICIENTS BETWEEN WIND DIRECTION AND PCB CONCENTRATION

STATION NO.	N	NNE	NE	ENE	E	ESE	SE	SSE	S	SSW	SW	WSW	W	WNW	NW	NNW
4 Fenceline	-0.213	-0.221	-0.045	-0.108	-0.070	0.348	0.231	0.132	0.117	0.140	0.123	-0.019	-0.021	0.200	-0.074	-0.258
5 "	-0.428	-0.297	-0.136	-0.223	-0.171	0.125	0.183	0.023	0.364	0.148	0.477	0.004	0.296	0.084	-0.186	-0.270
6 "	-0.212	-0.100	-0.190	-0.319	-0.255	-0.173	-0.124	0.309	0.654	0.259	0.319	0.207	0.107	-0.127	-0.370	-0.220
7 "	-0.305	-0.131	0.317	0.224	0.108	0.330	0.251	-0.018	0.108	-0.003	0.203	0.032	-0.128	-0.157	-0.280	-0.214
1 Residential	-0.333	-0.179	0.014	-0.167	-0.209	-0.033	-0.115	0.056	0.063	0.308	0.202	0.209	0.216	-0.034	-0.274	-0.298
2 "	-0.275	-0.182	-0.328	-0.333	-0.256	-0.055	-0.075	0.102	0.369	0.346	0.446	0.170	0.502	0.216	-0.219	-0.212
3 "	-0.077	-0.090	-0.153	-0.230	-0.190	-0.066	-0.039	-0.119	-0.163	0.528	-0.045	0.250	-0.016	0.090	0.023	0.063
8 "	-0.301	-0.185	0.105	0.103	-0.076	0.045	0.106	-0.077	0.307	0.185	0.307	0.217	0.180	0.039	-0.332	-0.247
9 "	-0.436	-0.326	0.059	-0.078	-0.101	0.025	0.009	0.222	0.396	0.425	0.323	0.271	0.280	0.137	-0.251	-0.413
10 "	0.098	0.256	-0.042	-0.060	-0.108	0.130	0.119	0.153	0.068	0.095	0.016	0.097	-0.203	-0.077	-0.161	-0.056
11 "	-0.458	-0.110	0.127	-0.083	-0.119	0.154	0.110	0.260	0.375	0.129	0.316	0.189	0.147	0.003	-0.359	-0.152

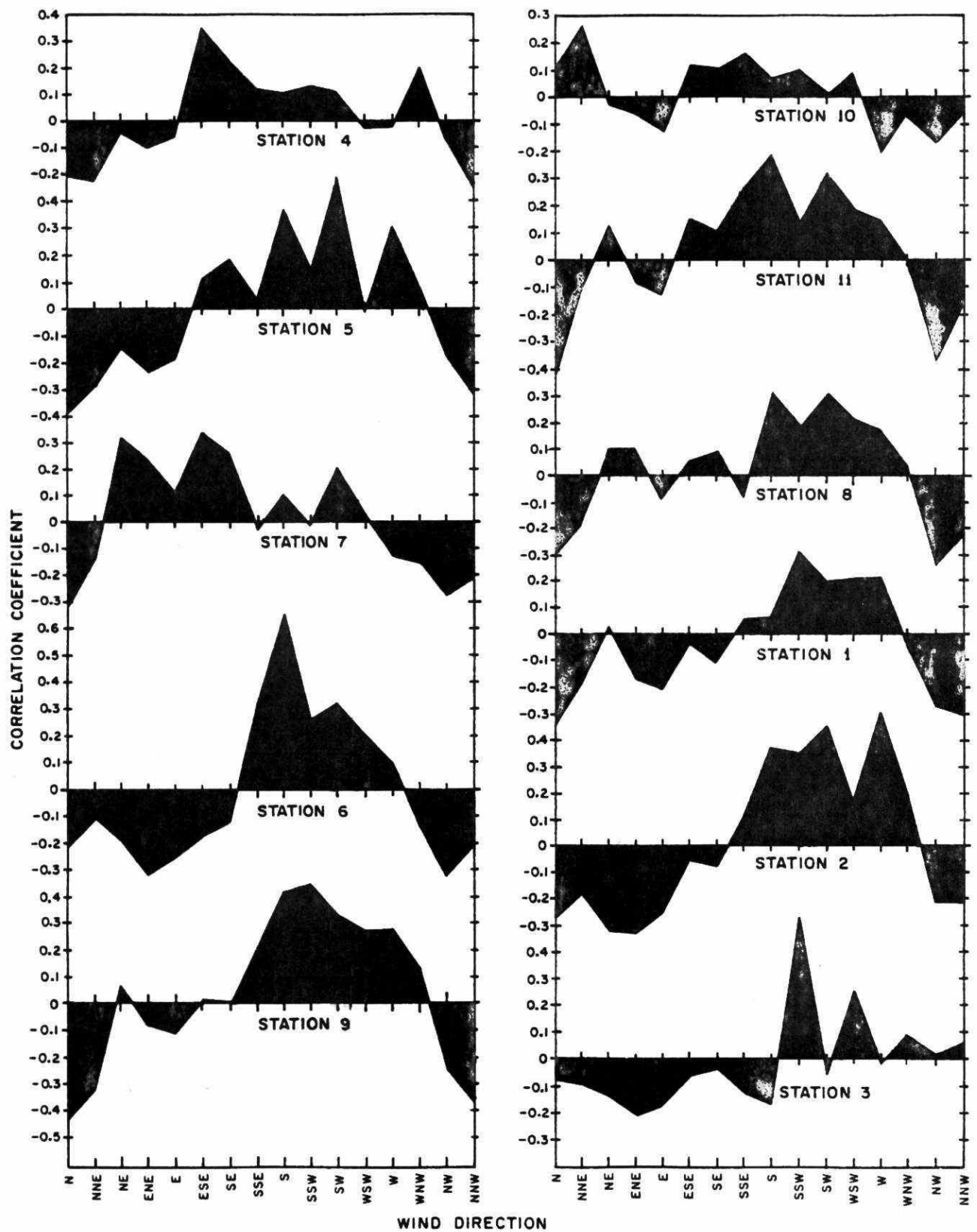


FIGURE 3.2 CORRELATION COEFFICIENTS OF FREQUENCY DISTRIBUTION OF TOTAL PCB CONCENTRATION WITH WIND DIRECTION .

correlation coefficients for westerly to southwesterly directions.

At S4 (southwest of St. Lawrence) there is also a southeasterly, and to a lesser extent, WNW component. Specific features of the results to be noted are:

- fence line sites (S5, S6, S7) correlate with known storage and handling areas
- general trend to positive values for W-SW directions reflects the transport of PCBs by the prevailing winds (Figure 2.1) The profiles at S1, S4 and S8 provide the most direct evidence that PCBs probably are being transported into the study area from more distant sources to the W-SW
- virtually all the stations in the NE sector of the survey area (S2, S3, S11, S10, S9) show SW contributions, with those aligned directly with the plants showing the most pronounced pattern. The levels measured at these sites presumably reflect the contribution of both remote and local sources and the relative importance of these two contributions will be discussed in further detail below
- the previously discussed local interferences at S3 results in a poorer correlation than at S2 and S9
- a relatively weak correlation is observed at S10, with the most pronounced contribution appearing to arise from the NNE, again indicating the possibility of local interferences.

The correlation data from Figure 3.2 is presented in the form of wind roses in Figures 3.3 and 3.4, in order to provide a more direct indication of the directional patterns at each station. A constant value of 0.5 has been added to all correlation coefficients so that they could be presented in this manner. Data for S4 is presented in both figures to permit direct comparison. It can be tentatively concluded that both local and remote sources contribute to the PCB levels measured in the survey area. The magnitude of contributions by remote sources to the southwest is best indicated by the concentrations measured at S1, S4 and S8. On the other hand, direct and significant contribution to the plant

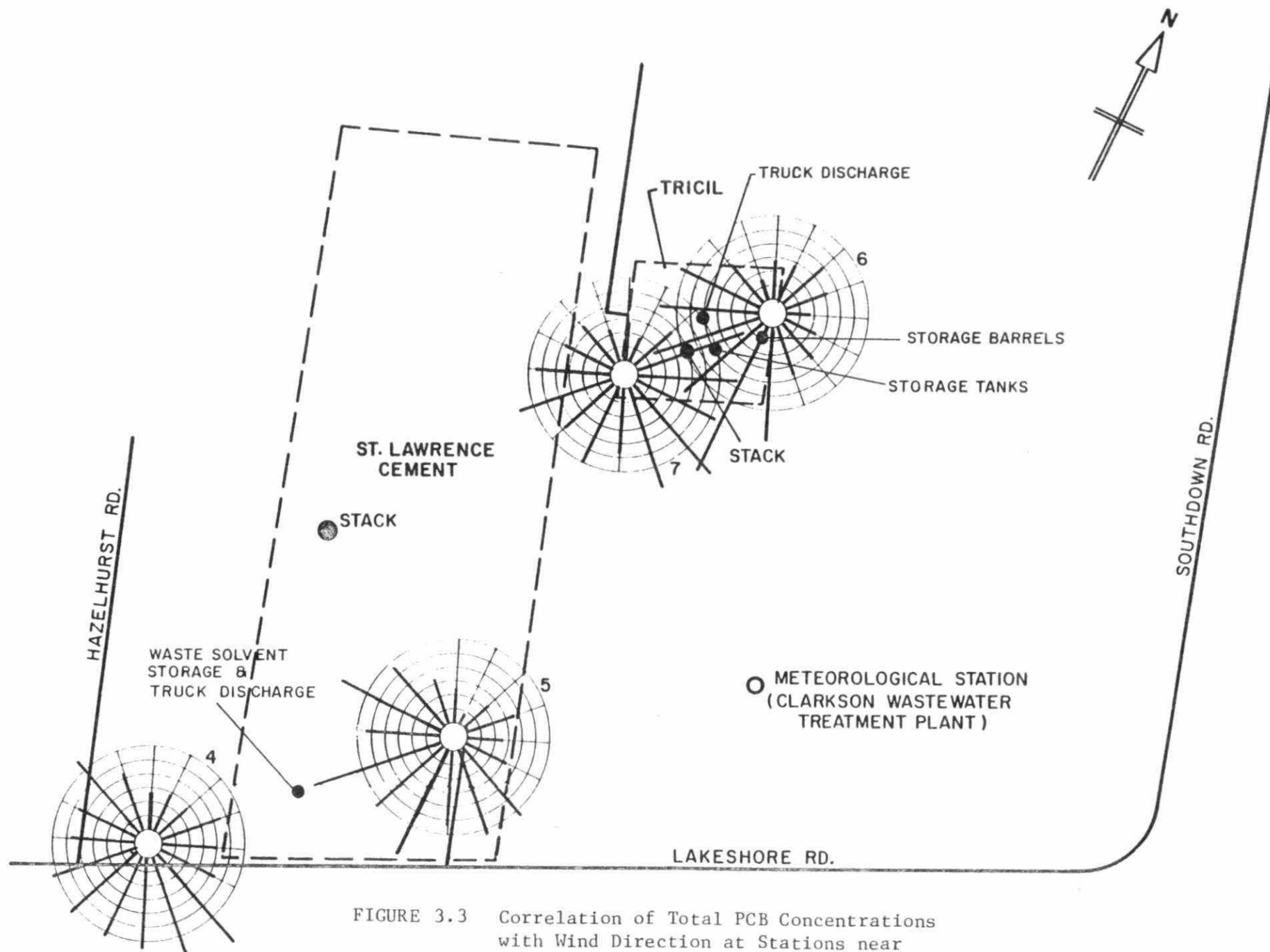


FIGURE 3.3 Correlation of Total PCB Concentrations with Wind Direction at Stations near Industrial Properties

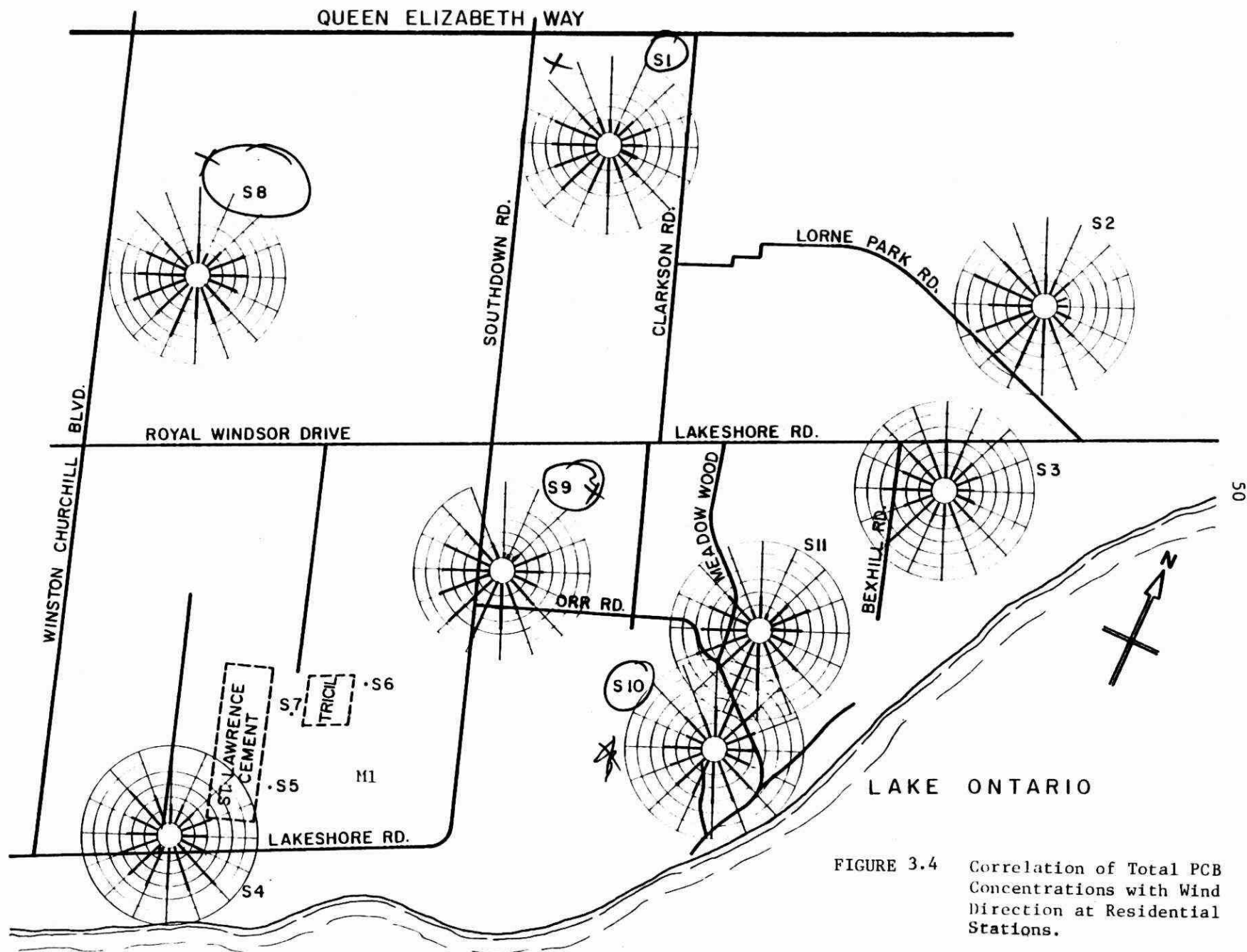


FIGURE 3.4 Correlation of Total PCB Concentrations with Wind Direction at Residential Stations.

property sites is apparent, particularly at S6. The more pronounced correlations at S2, S3, S9 and S11 appear to reflect the combined contribution of both local and remote sources. As mentioned above, the overall average concentration at these sites (approx. 10.7 ng.m^{-3}) is not significantly different from that for S1, S4 and S8 (9.3 ng.m^{-3}) and so it would appear that only a relatively minor contribution is made by local emissions to these residential sites. This conclusion also is supported by the previously discussed evidence of local interferences at S2 and S3.

Wind speed also can be important in determining the pollutant concentrations observed at a particular site. Correlation coefficients have been calculated for four wind speed classes and results are summarized in Table 3.4. Relatively weak correlations are observed in all cases but the tendency is for positive values to concur with the lower wind speeds. This may simply reflect a greater tendency of PCBs from both local and remote sources to accumulate under the relatively stagnant conditions represented by the lowest wind speed class.

The qualitative aspects of this statistical approach must be appreciated when assessing the significance of the directional patterns discussed above. Because of the nature of the data being evaluated, considerable scatter exists in the correlation plots and this is reflected in the relatively low r values shown in Table 3.3. With 50 degrees of freedom, the correlation coefficient should be greater than 0.27 to be significant at the 95% confidence level. Inspection of Figure 3.2 confirms that the positive r values for the predominant directions (i.e., southwesterly directions in most instances) generally are greater than 0.27. Furthermore, for the purposes of this evaluation, it is only the relative magnitude of the coefficients for the various wind directions that is important. Individual data for two points with relatively large r values (south at S6 and SSW at S9) are shown in Figures 3.5 and 3.6 to provide a proper perspective of this feature of the results.

TABLE 3.4 CORRELATION COEFFICIENTS BETWEEN WIND SPEED CLASSES
AND AMBIENT PCB CONCENTRATION

STATION NO.	Wind Speed Categories (km/hr)			
	4.8	4.9-11.3	11.4-19.3	19.4
4 Fenceline	0.162	0.024	-0.275	-0.266
5 "	0.069	-0.073	-0.200	-0.368
6 "	-0.004	0.056	0.040	-0.290
7 "	-0.019	-0.002	-0.329	-0.221
1 Residential	-0.170	0.082	-0.218	-0.231
2 "	0.179	0.140	-0.159	-0.131
3 "	-0.188	-0.028	0.165	0.222
8 "	0.231	0.105	-0.206	-0.250
9 "	0.161	0.310	-0.270	-0.273
10 "	0.025	-0.077	0.118	-0.057
11 "	0.133	0.222	-0.153	-0.374

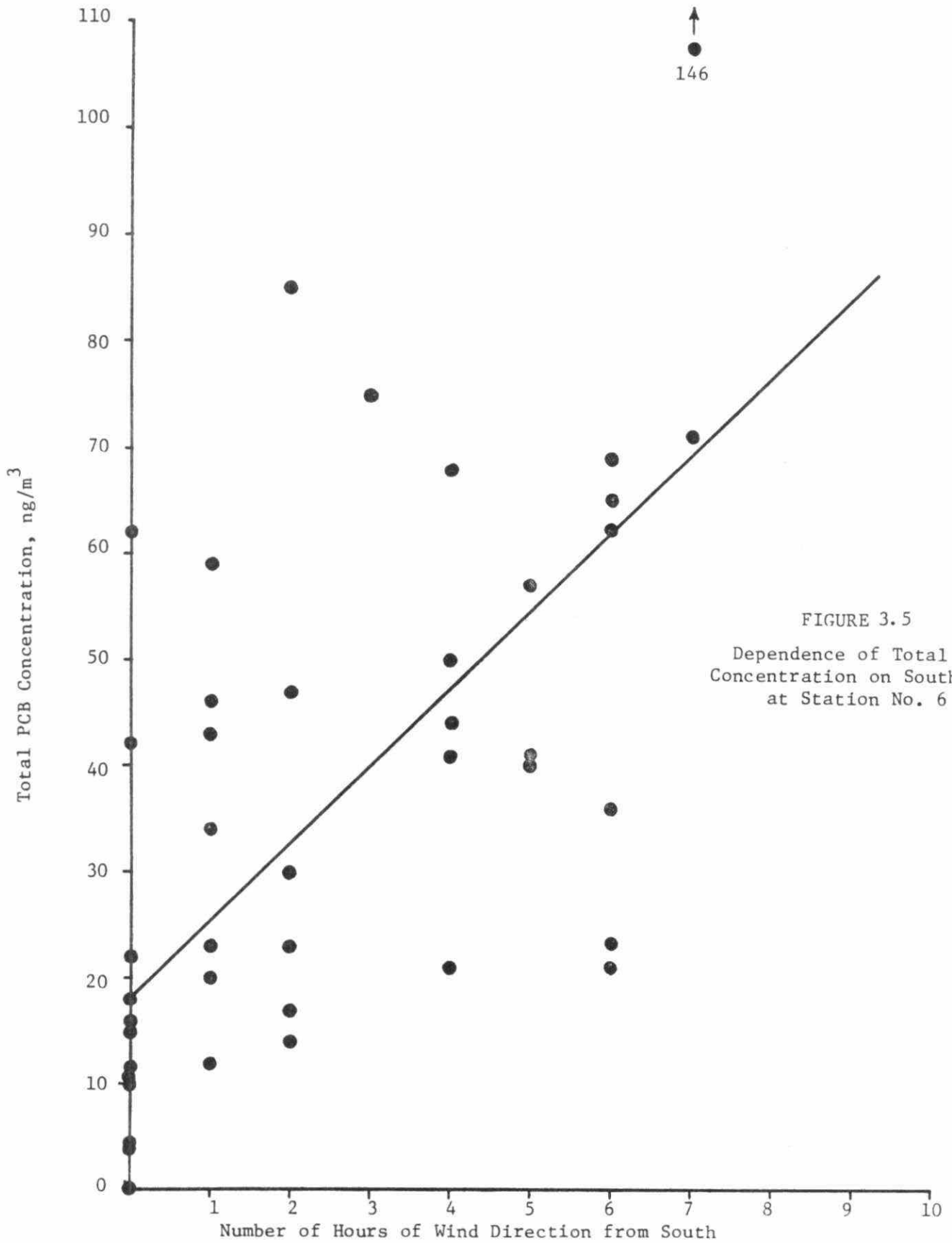


FIGURE 3.5
Dependence of Total PCB
Concentration on South Wind
at Station No. 6

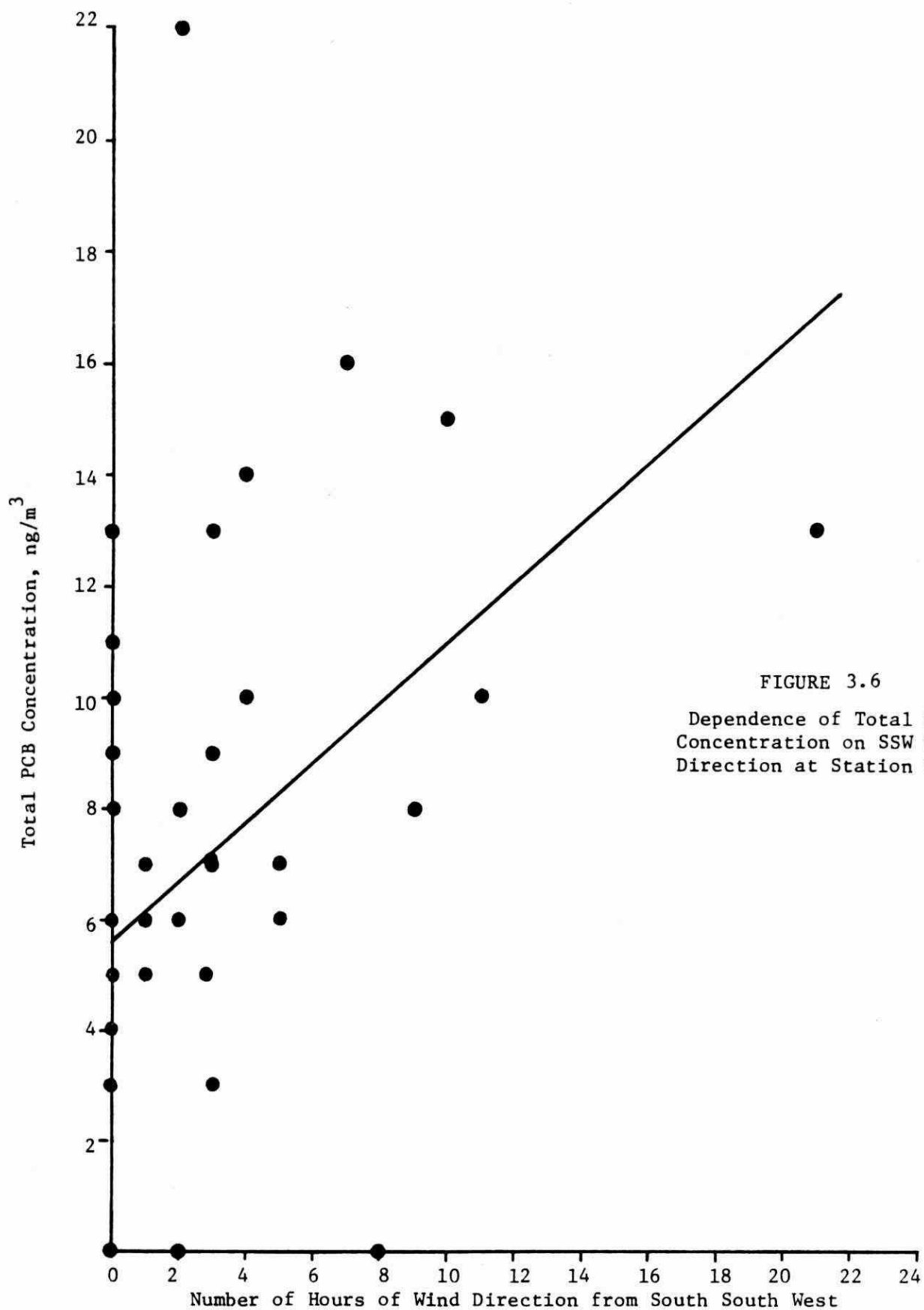


FIGURE 3.6

Dependence of Total PCB
Concentration on SSW Wind
Direction at Station No. 9

Wind data (43 m level) also were obtained from Ontario Hydro for their monitoring site approximately 2 km northwest of Lakeview Generating Station. Higher level winds were considered particularly relevant to the stack emissions and the above calculations were repeated using these data. The results were very similar and the profiles of Figure 3.2 did not change significantly confirming the conclusions made using low level winds.

3.3 PCB Isomer Profiles

In a further attempt to explain the rather large variations in levels at the individual sites and to substantiate the possible importance of positive interferences by non-PCB material in many of the anomalously high samples, the isomeric patterns for all samples were evaluated in considerable detail. As described in a previous section, a total of 12 gas chromatographic peaks were measured, and these represented 16 PCB isomers. The association of certain peaks with anomalously high "total" PCB values at some sites was suspected as a result of this inspection of individual isomer profiles. In order to obtain a more general impression of trends in isomeric patterns, and the nature of suspected interferences resulting in anomalous values, average isomeric profiles for the blank samples and each monitoring site have been calculated and are shown in Table 3.5. The profiles were calculated in terms of the weight of each isomer found in the sample, rather than as ambient concentrations, to permit comparison with blank levels and to reduce as much as possible the very extensive calculations required to determine the average values and the standard deviations for each isomer at each site.

The average isomeric profiles plotted as bar charts in Figure 3.7 have proven extremely helpful in assessing the variations in isomeric patterns which occurred on a day to day basis and from station to station. Several conclusions can be made on the basis of these average profiles:

- ambient air samples do show consistent profiles with peaks 5, 6, 7 and 8 predominating at all stations except S6. The average relative amounts of these isomers also shows a consistent pattern, with 5 and 8 generally being the largest peaks

TABLE 3.5

STATISTICAL SUMMARY OF PCB ISOMER PATTERNS (ng/sample)

Station No.		PCB ISOMER PEAKS												TOTAL
		1	2	3	4	5	6	7	8	9	10	11	12	
Blank	A.M.	0	0	0.4	1.4	1.8	3.4	2.7	1.7	1.0	1.3	0.4	1.1	1.1
	S.D.	0	0	1.62	3.99	8.72	5.09	5.30	5.17	19.19	9.39	1.29	2.67	.8
	R.S.D.	-	-	1.27	2.00	2.95	2.26	2.30	2.27	4.38	3.06	1.14	1.63	0.8
Fenceline Sites														
4	A.M.	0.4	7.0	1.8	5.4	32	9.0	21	50	2.5	8.6	5.6	1.5	9.9
	S.D.	2.00	26.89	6.11	6.34	33.83	9.85	34.46	102.56	6.45	13.81	12.59	2.06	12.
	R.S.D.	5.0	3.8	3.4	1.2	1.1	1.1	1.6	2.1	2.6	1.6	2.2	1.4	1.2
5	A.M.	1.2	14	9.0	8.8	30	8.0	15	31	2.7	5.5	3.4	2.1	8.8
	S.D.	5.39	27.52	15.9	5.68	24.46	6.26	18.32	45.61	5.80	5.90	4.03	2.4	7.0
	R.S.D.	4.5	2.0	1.8	0.6	0.8	0.8	1.2	1.5	2.1	1.8	1.2	1.1	0.8
6	A.M.	2.1	130	47	21	38	22	34	27	6.7	33	10	14	36
	S.D.	14.57	145.02	30.85	13.40	20.59	15.10	27.41	34.21	11.16	79.62	8.99	82.78	28.9
	R.S.D.	6.9	1.1	0.7	0.6	0.5	0.7	0.8	1.3	1.7	0.9	0.9	5.8	0.8
7	A.M.	0.9	12	10	13	25	14	20	36	2.3	9.8	3.7	3.0	12
	S.D.	3.67	29.99	20.87	17.51	18.74	16.29	17.15	49.10	6.36	10.20	4.07	6.50	11.4
	R.S.D.	4.1	2.5	2.0	1.3	0.7	1.2	0.8	1.4	2.8	1.0	1.1	2.2	0.9
Residential Sites														
1	A.M.	0.2	0	1.0	5.5	28	12	33	39	3.3	15	25	12	12
	S.D.	1.54	0	0.70	13.16	29.90	11.14	33.2	42.31	6.75	11.62	19.15	54.96	8.8
	R.S.D.	7.7	-	0.7	2.4	1.1	0.9	1.0	1.1	2.0	0.8	0.8	4.6	0.8
2	A.M.	1.5	2.4	1.5	1.1	41	15	55	38	3.5	13	3.3	1.0	13
	S.D.	6.39	11.1	7.84	3.53	29.81	16.55	41.05	33.21	7.14	10.82	2.41	2.23	8.9
	R.S.D.	4.3	4.6	5.2	3.2	0.7	1.1	0.8	0.9	2.0	0.8	0.7	2.2	0.7
3	A.M.	0.2	1.5	1.6	6.3	56	18	65	54	4.5	21	4.3	3.1	17
	S.D.	1.27	10.75	8.97	19.45	79.40	27.23	93.68	73.89	8.19	37.00	3.81	6.60	20.4
	R.S.D.	6.4	7.2	5.6	3.1	1.4	1.5	1.4	1.4	1.8	1.7	0.9	2.1	1.2
8	A.M.	0.3	0.6	0.1	5.1	19	8.2	15	30	3.2	7.8	3.0	2.2	5.5
	S.D.	1.84	4.38	0.42	7.92	12.79	7.43	9.71	31.07	11.91	7.71	4.17	5.34	5.3
	R.S.D.	6.1	7.1	7.0	1.6	0.7	0.9	0.6	1.0	3.7	1.0	1.4	2.4	1.0
9	A.M.	0.2	5.2	0.1	5.0	24	7.4	15	34	2.5	7.3	4.9	1.3	6.6
	S.D.	1.26	20.81	0.84	7.63	19.75	5.28	9.30	25.56	6.55	6.36	4.86	1.60	5.1
	R.S.D.	6.3	4.0	7.0	1.5	0.8	0.7	0.6	0.8	2.6	0.9	1.0	1.2	0.8
10	A.M.	0.6	40	0.3	5.4	23	6.5	16	23	2.7	6.5	1.7	1.8	8.9
	S.D.	3.18	74.89	1.20	5.85	16.34	6.27	21.89	17.83	5.68	3.73	2.03	2.81	6.5
	R.S.D.	5.3	1.9	4.0	1.1	0.7	1.0	1.4	0.8	2.1	0.6	1.2	1.6	0.7
11	A.M.	0.9	1.8	0.2	6.4	15	9.0	15	26	1.6	6.7	2.5	2.4	6.7
	S.D.	5.44	13.16	0.78	5.17	10.04	4.62	5.76	19.33	3.83	5.68	2.72	4.09	3.4
	R.S.D.	5.9	7.2	4.9	0.8	0.7	0.5	0.4	0.7	2.4	0.8	1.1	1.7	0.5

A.M. = Arithmetic Mean (ng) S.D. = Standard Deviation R.S.D. = Relative Standard Deviation ($\frac{S.D.}{A.M.}$)

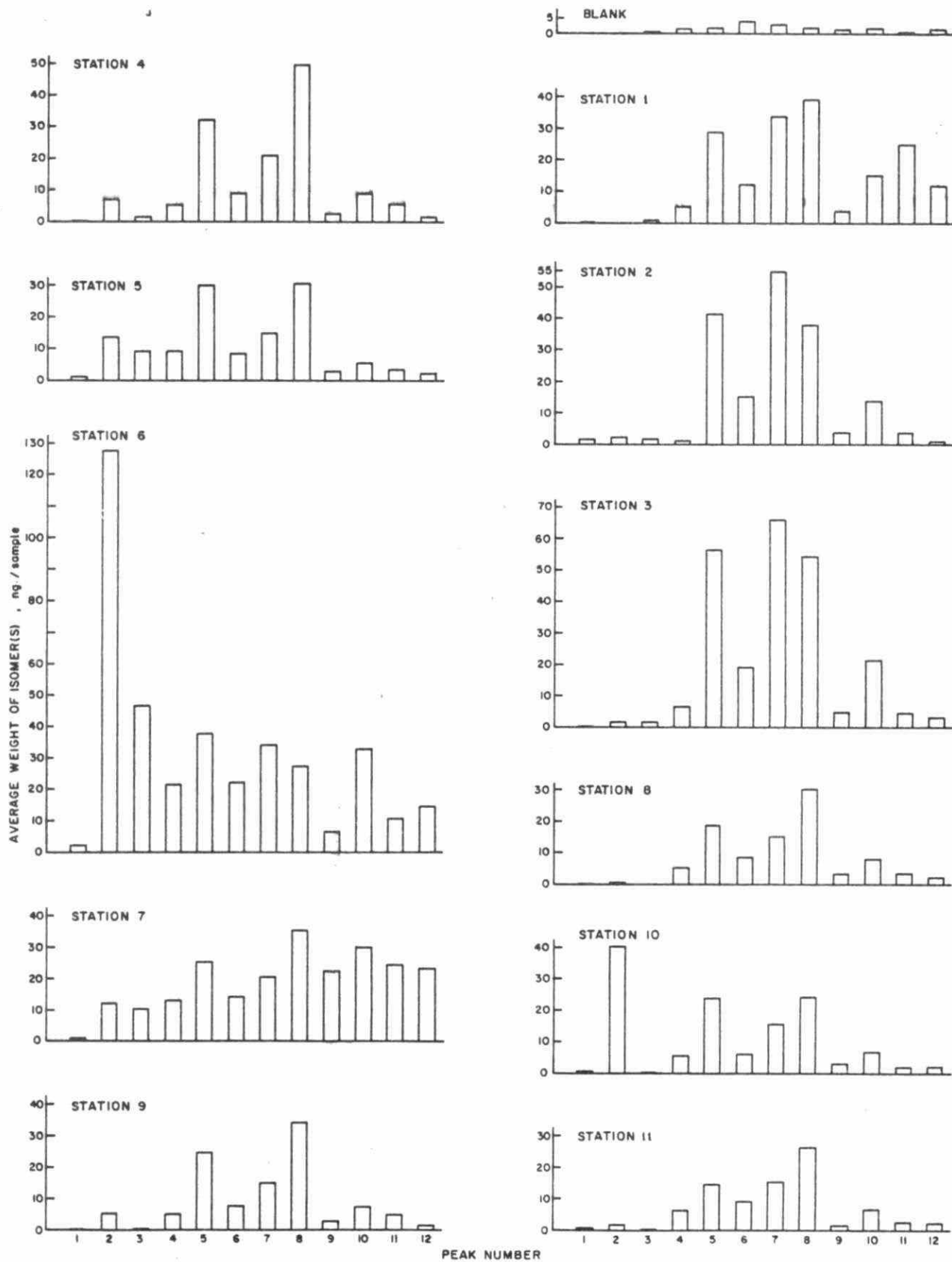


FIGURE 3.7 AVERAGE PCB ISOMER PROFILES FOR SAMPLING STATIONS

- peaks 9 to 12 generally are present in lesser but significant proportions, with peak 10 predominating in this group
- peaks 1 - 4 show considerable variation from station to station and represent only a minor portion of the total sample
- unusual patterns identified include:
 - 1) a very large peak 2, plus moderate levels of 3 and 4, at S6
 - 2) a very distinct peak 2 at S10
 - 3) a larger than average peak 10 at S6, and to a lesser extent, at S3.

It is tentatively concluded that these average profiles can be used to define a "typical" profile for ambient PCB levels in terms of the 12 GC peaks measured in these studies. Exclusion of the anomalous features mentioned above suggests a profile dominated by peaks 5, 6, 7, 8 with 5 and 8 the largest peaks. Peaks 9 to 12 are generally less than 25% of the 5 to 8 group, but also occur in a fairly consistent pattern. Peaks 1 to 4 generally make only a minor contribution to the total weight of PCB in the sample. It is concluded that large variations from this normal pattern (such as peak 2 at S6 and S10) represent positive interferences by non-PCB materials. While atmospheric processes no doubt can alter PCB isomer patterns from those observed for commercial mixtures, it is extremely unlikely that large variations such as these can be attributed to isomer dependent atmospheric effects. Isomer profiles of six standard Aroclor mixtures, which have been analyzed and described in section 2.3.4, are plotted as bar charts (Figure 3.7). By combining these six Aroclors arbitrarily as equal portions and averaging the isomer weights for each of the twelve peaks, the bottom profile depicts an overall pattern of the combined mixture. An overlay transparency has been included in a separate envelope (last page) to permit the comparison of isomeric patterns between known PCBs and the patterns obtained at each station. Although it is highly unlikely that such a combination would occur in the atmosphere, similarities with station profiles were found particularly for the pattern of peaks 9 - 12.

In order to further quantify the variations in the total PCB levels and isomer patterns occurring at each site, standard deviations have been calculated for each gas chromatograph peak and are summarized in Table 3.5. Relative standard deviations (standard deviation/average value) have also been calculated to permit a direct estimate of the variation in levels to be made independent of the absolute amounts of each isomer. The higher coefficients, which indicate wider variation, were generally found for peaks 1, 2, 3 and sometimes 4. Except for occasional anomalies, the results of the calculations tended to statistically confirm the qualitative conclusions that peaks 5 to 8, and to a lesser extent peaks 9 to 12, generally show a consistent isomeric pattern. When expressed as percentage variability, the three groups of isomers ranged from 70 - 770%, 40 - 210% and 60 - 580%, respectively. The high coefficient for peak 12 of the isomeric pattern obtained at S1 is mostly attributable to a single high value on the first day of sampling (June 5-6) which accounted for 80% of the 48 ng.m^{-3} total PCB concentration found that day. This also held true for peak 12 measured at S6 (June 6-7), which accounted for 70% of the total concentration. These high individual peaks are definitely considered to be outliers and presumably are due to local interferences. Unusual isomeric patterns based on the average isomer weight (i.e., peaks 2 at S6 and S10, and peak 10 at S3 as previously mentioned) result in high standard deviations but low relative standard deviations as the latter are influenced considerably by the magnitude of both the average isomer weight and the standard deviation. This is shown more clearly for peaks 1 and 2 at S10. In this case, the isomers of peak 1 were detected only on two of the 51 days which tended to result in a low average isomer weight and a high coefficient of variation. On the other hand, peak 2 was detected on 15 of the 51 days with sufficient magnitude on these days to elevate the average isomer weight and subsequently decrease the coefficient of variation even though a large standard deviation existed for this isomer. The same held true for peaks 1 and 2 at S6. The station which showed the largest variability, based on total PCB concentration, was S3 and again local interferences were suspected. No positive correlations between high individual isomer weights and predominant wind directions were apparent.

4. CONCLUSIONS

The primary objective of this study was to provide a quantitative assessment of ambient PCB concentrations in the vicinity of the St. Lawrence Cement and Tricil plants located in Mississauga, and to assess the importance of the contribution made by these plants to these levels. Several specific conclusions have been drawn from the results:

- average ambient concentrations ranged from a low of 6 ng.m^{-3} in the residential areas to a high of 36 ng.m^{-3} on the Tricil property
- both the observed PCB isomer distributions and several features of the aerometric data suggest that positive interferences can occur, and indicate the need to confirm GC/EC results with other techniques. However, on the basis of observed isomeric patterns, such interferences were probably a significant factor only at the site NE of the Tricil plant and at three of the residential sites (S2, S3, S10) and would increase the measured value
- average PCB concentration at the residential sites ranged from $6\text{--}12 \text{ ng.m}^{-3}$. These must be considered as upper limit values until confirmatory results are obtained from other ongoing studies.
- comparison of the PCB levels at upwind and downwind sites and correlations of PCB concentrations with wind direction indicate that emissions from St. Lawrence Cement and Tricil do not make a measurable contribution to ambient PCB levels in the residential areas surrounding the plants
- on property sites show evidence of a contribution from the industrial plants which appear to arise from storage and handling operations
- the results suggest that PCBs may be transported into the area from more remote sources to the southwest, in agreement with the generally held concept that atmospheric transport is an important pathway whereby PCBs are distributed throughout the atmosphere.

In general, this study confirms the ubiquitous nature of PCBs in the atmosphere and provides further evidence of the need for more specific analytical techniques. The results indicate that fugitive emissions from the St. Lawrence Cement and Tricil plants contribute to levels within the plant property, but do not show any evidence of a measurable contribution to ambient PCB levels in the surrounding residential areas.



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